U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-266 224

Industrial Process Profiles for Environmental Use: Chapter 5 Basic Petrochemicals Industry

Radian Corp, Austin, Tex

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

Jan 77

PB 266 224

EPA-600/2-77-023e
January 1977

Environmental Protection Technology Series

UNITED STATES · ENVIRONMENTAL PROTECTION AGENCY

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

EPA REVIEW NOTICE

This report has been reviewed by the U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policy of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-77-023e	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Industrial Process Profiles for Environmental Use: Chapter 5. Basic Petrochemicals Industry		5. REPORT DATE January 1977 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) T. B. Parsons, C. M. Thompson, and G. E. Wilkins		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation P.O. Box 9948 Austin, Texas 78766		10. PROGRAM ELEMENT NO. 1AB015; ROAP 21AFH-025 11. CONTRACT/GRANT NO. 68-02-1319, Task 34
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Initial; 8/75-11/76 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES Project Officer I.A. Jefcoat is no longer with EPA: contact G. Tucker (IERL-RTP), Mail Drop 63, 919/549-8411 Ext 2745.

16. ABSTRACT The catalog was developed to aid in defining the environmental impacts of U.S. industrial activity. Entries for each industry are in consistent format and form separate chapters of the catalog. The basic petroleum industry includes companies that treat hydrocarbon streams from the petroleum refining industry, as well as natural gas liquids from the oil and gas production industry. From these raw materials, feedstocks are produced for the organic chemicals industry. The products are pure or mixed chemicals for use as solvents or chemical intermediates. This industry is described by six operations composed of related processes. Four chemical trees, six process flow sheets, and 28 process descriptions characterize the industry. For each process description, available data is presented on input materials, operating parameters, utility requirements, and waste streams. Related information, provided as appendices, includes company, raw material, and product data.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Solvents	Process Assessment	13B	11K
Industrial Processes		Environmental Impact	13H	
Chemical Engineering		Basic Petrochemical Industry	07A	
Petrochemistry			08G	
Hydrocarbons		Chemical Intermediates	07C	
Natural Gas Liquids			21D	

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 155
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE PC A08 / MF A01

Form 2220-1 (9-73)

1a

EPA-600/2-77-023e
January 1977

INDUSTRIAL PROCESS PROFILES FOR ENVIRONMENTAL USE:
CHAPTER 5. BASIC PETROCHEMICALS INDUSTRY

by

T.B. Parsons, C.M. Thompson, and G.E. Wilkins

Radian Corporation
P.O. Box 9948
Austin, Texas 78766

Contract No. 68-02-1319, Task 34
ROAP No. 21AFH-025
Program Element No. 1AB015

EPA Project Officer: I.A. Jefcoat

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

TABLE OF CONTENTS

CHAPTER 5

Page

INDUSTRY DESCRIPTION.. 1
Raw Materials.. 9
Products.. 9
Companies.. 14
Environmental Impact.. 15
Bibliography.. 20

INDUSTRY ANALYSIS.. 22
Olefins Production Processes.. 23
Process No. 1. Thermal Cracking.. 28
Process No. 2. Oil Quenching.. 32
Process No. 3. Water Quenching.. 34
Process No. 4. Compression.. 36
Process No. 5. Acid Gas Removal.. 38
Process No. 6. Water Removal.. 40
Process No. 7. Demethanation.. 41
Process No. 8. C_2 Separation.. 43
Process No. 9. C_3 Separation.. 46
Process No.10. C_4 Separation.. 48
Process No.11. Heavy Fractionation.. 49
Butadiene Production Processes.. 50
Process No.12. Separation and Purification.. 53
Process No.13. Butane Dehydrogenation.. 57
Process No.14. Butenes Dehydrogenation.. 60
BTX Production Processes.. 63
Process No.15. Hydrotreating.. 65
Process No.16. Aromatics Extraction.. 70
Process No.17. C_6-C_9+ Aromatics Separation.. 74
Process No.18. C_8 Aromatics Fractionation.. 76
Process No.19. Para-xylene Crystallization.. 78
Process No.20. Para-xylene Adsorption.. 81

TABLE OF CONTENTS (continued)

Page

Process No.21. C_8 Aromatics Isomerization 83
Process No.22. Toluene Disproportionation/Transalkylation 86
Process No.23. Hydrodealkylation 89
Naphthalene Production Processes 93
Process No.24. Extraction of Dicyclic Aromatics 95
Process No.25. Hydrodealkylation to Produce Napthalene 98
Cresols and Cresylic Acids Production Processes 102
Process No.26. Acidification 104
Process No.27. Product Recovery 107
Normal Paraffin Production Processes 109
Process No.28. Separation of Normal Paraffins 111

APPENDIX A - Raw Materials 115

APPENDIX B - Products 117

APPENDIX C - Producers of Basic Petrochemicals and Production Locations 119

LIST OF FIGURES

CHAPTER 5

Figure Page

1 PETROCHEMICAL USE OF ETHYLENE IN 1973........................10

2 PETROCHEMICAL USE OF BENZENE IN 1973.........................11

3 PETROCHEMICAL USE OF BUTADIENE IN 1973.......................12

4 PETROCHEMICAL USE OF PROPYLENE IN 1973.......................13

5 OLEFINS PRODUCTION PROCESSES.................................24

6 BUTADIENE PRODUCTION PROCESSES...............................51

7 BTX PRODUCTION PROCESSES.....................................64

8 NAPHTHALENE PRODUCTION PROCESSES.............................94

9 CRESOLS AND CRESYLIC ACIDS PRODUCTION PROCESSES.............103

10 SEPARATION OF NORMAL PARAFFINS..............................110

LIST OF TABLES

CHAPTER 5

Table Page

1 OPERATIONS IN THE BASIC PETROCHEMICAL INDUSTRY....................2

2 1974 PRODUCTION OF BASIC PETROCHEMICALS..............................3

3 GEOGRAPHIC LOCATION OF BASIC PETROCHEMICAL MANUFACTURING FACILITIES.................................5

4 PRODUCTS FROM CRUDE OIL CRACKING TO PRODUCE 500 Gg (ONE BILLION POUNDS) ETHYLENE PER YEAR........................6

5 EXAMPLE PRODUCT SLATE FROM COAL UTILIZATION FOR PETROCHEMICAL FEEDSTOCKS..................................6

6 1974 PREDICTIONS FOR FUTURE DEMAND AND GROWTH RATE OF BASIC PETROCHEMICALS.................................7

7 1973 FEEDSTOCK REQUIREMENTS OF THE BASIC PETROCHEMICALS INDUSTRY...8

8 BASIC PETROCHEMICAL PRODUCTION BY PETROLEUM REFINERS IN 1974...14

9 LARGE VOLUME PETROCHEMICAL PRODUCERS..............................16

10 UTILITY REQUIREMENTS FOR AN ETHYLENE PLANT.......................23

11 ESTIMATED HYDROCARBON LOSSES FROM AN ETHYLENE PLANT PRODUCING 227 Gg (500 MILLION LB)/YR.........................25

12 WASTEWATER COMPOSITION FROM OLEFIN PLANTS........................26

13 TYPICAL EQUIPMENT REQUIREMENTS FOR A 500 Gg/YR NAPHTHA CRACKER...27

14 STEAM-TO-HYDROCARBON RATIOS.......................................28

15 FEEDSTOCK AND PRODUCTION DATA.....................................29

16 HEAT RECOVERY IN TRANSFER LINE HEAT EXCHANGERS....................29

17 COMPOSITION OF A REFINERY GAS.....................................36

18 WASTE CAUSTIC STREAM COMPOSITION 39

19 TYPICAL DEMETHANIZER FEEDS..41

20 TYPICAL ETHYLENE PRODUCT SPECIFICATIONS...........................43

21 COMPOSITION OF WASTE FROM A BUTADIENE PLANT......................52

22 BUTADIENE YIELDS FROM THERMAL CRACKING...........................54

23 ACETYLENICS CONTENT OF VARIOUS C_4 STREAMS......................54

24 WASTEWATER FROM BUTADIENE PLANTS..................................55

25 OPERATING PARAMETERS FOR DEHYDROGENATION OF BUTENES...61

LIST OF TABLES (continued)

Table Page

26 HYDROCARBONS IN TYPICAL PYROLYSIS GASOLINE CONTAINING 70% AROMATICS....66

27 DESIGN CASE COMPOSITION OF FEED AND PRODUCT FROM TWO-STAGE HYDROGENATION OF PYROLYSIS GASOLINE....66

28 UTILITY REQUIREMENTS FOR 182,000 METRIC TON/YR TWO-STAGE PYROLYSIS GASOLINE HYDROTREATER....67

29 CHARACTERISTICS OF WASTEWATER FROM TWO-STAGE HYDROTREATING OF PYROLYSIS GASOLINE....68

30 TYPICAL AROMATICS CONTENT IN REFORMATE....71

31 OPERATING PARAMETERS FOR UDEX AND SULFOLANE AROMATICS EXTRACTION PROCESSES....71

32 UTILITY REQUIREMENTS FOR UDEX AND SULFOLANE AROMATICS EXTRACTION PROCESSES....72

33 TYPICAL COMPOSITION OF C_8 AROMATICS MIXTURES FROM VARIOUS SOURCES....76

34 UTILITY REQUIREMENTS FOR PARA-XYLENE CRYSTALLIZATION....79

35 UTILITY REQUIREMENTS FOR COMBINED ADSORPTION (AROMAX PROCESS) AND ISOMERIZATION PROCESS PRODUCING 100 Gg/YEAR PARA-XYLENE....81

36 OPERATING CONDITIONS FOR COMMERCIAL C_8 AROMATICS ISOMERIZATION PROCESSES....84

37 UTILITY REQUIREMENTS FOR COMBINED XYLENE CRYSTALLIZATION-ISOMERIZATION PROCESS....84

38 VARIATIONS OF DISPROPORTIONATION/TRANSALKYLATION PRODUCT RATIOS WITH C_9 CONTENT OF FEED....87

39 UTILITY REQUIREMENTS FOR VAPOR PHASE CATALYTIC TOLUENE DISPROPORTIONATION WITH C_9 RECYCLE....87

40 TYPICAL COMPOSITION OF FEEDSTOCKS FOR HOUDRY HYDRODEALKYLATION PROCESS....90

41 UTILITY CONSUMPTION RATES FOR BENZENE PRODUCTION FROM TOLUENE BY THE HYDEAL PROCESS....91

42 UTILITY REQUIREMENTS FOR THE HOUDRY CATALYTIC HYDRODEALKYLATION PROCESS....91

43 STREAM COMPOSITIONS FOR EXTRACTION PROCESS....95

44 UTILITY REQUIREMENTS FOR EXTRACTION OF ALKYL NAPHTHALENES FROM DIFFERENT FEEDSTOCKS....96

45 TYPICAL COMPOSITION OF NAPHTHALENE CHARGE STOCKS....98

LIST OF TABLES (continued)

Table Page

46 PRODUCT YIELDS FROM THE HYDEAL PROCESS....................................99

47 UTILITY REQUIREMENTS FOR THE HYDEAL PROCESS..........................99

48 TYPICAL COMPOSITION OF CAUSTIC STREAM..................................105

49 PHENOL CONTENT OF AQUEOUS WASTES FROM SPRINGING..................106

50 UTILITY REQUIREMENTS FOR ISO SIV PROCESS.................................112

A-1 HYDROCARBON RAW MATERIALS FOR THE BASIC PETROCHEMICALS INDUSTRY..116

B-1 PRODUCTS AND BY-PRODUCTS OF THE BASIC PETROCHEMICALS INDUSTRY..118

C-1 BENZENE PRODUCERS..120

C-2 BUTADIENE PRODUCERS...124

C-3 CRESOLS AND CRESYLIC ACIDS PRODUCERS..............................126

C-4 ETHYLENE PRODUCERS...127

C-5 NAPHTHALENE PRODUCERS..130

C-6 MIXED XYLENES PRODUCERS..131

C-7 NORMAL PARAFFINS PRODUCERS...133

C-8 PROPYLENE PRODUCERS...134

C-9 TOLUENE PRODUCERS..138

C-10 BASIC PETROCHEMICAL PRODUCTION SITES DIRECTLY ASSOCIATED WITH PETROLEUM REFINERIES....................................141

C-11 BASIC PETROCHEMICAL PRODUCTION SITES NOT DIRECTLY ASSOCIATED WITH A PETROLEUM REFINERY.....................................144

BASIC PETROCHEMICALS INDUSTRY

INDUSTRY DESCRIPTION

The basic petrochemicals industry described in this chapter includes companies which treat hydrocarbon streams from the petroleum refining industry (Chapter 3) and natural gas liquids from the oil and gas production industry (Chapter 2). These raw materials are used to produce feedstocks for the organic chemical industry including benzene, the butylenes, cresols and cresylic acids, ethylene, naphthalene, paraffins, propylene, toluene, and xylenes. The products are pure or mixed chemicals for use as solvents or chemical intermediates. Other product streams are captively consumed or used as feedstocks for certain processes within the refining industry. The industry is very difficult to define because its operations are "intertwined functionally or physically with the inorganic sector of the chemical industry, with downstream (manufacturing,) fabrication or compounding activities, or with the petroleum refining industry. (This results in) mixing of vertical operating steps in official statistics."*

The processes conducted in the basic petrochemicals industry are mainly separation and purification processes. Some chemical conversion processes such as cracking, hydrogenation, isomerization, and disproportionation are carried out. As defined in Chapter 1, a process converts a raw material into products, by-products, intermediate products, or waste streams. Six groups of related processes, termed operations, are employed by the industry. Table 1 lists the six operations along with their raw materials and products. Each of the operations listed in Table 1 is described in detail on a separate flow sheet containing a collection of processes which are indicated by numbered boxes. A process description was prepared for each process in the numbered boxes.

The 1975 Directory of Chemical Producers indicates that there are some 107 facilities at which basic petrochemicals are produced from refinery streams or natural gas liquids. Sixty-five percent of these facilities are closely associated with refineries, while the other thirty-five percent of the locations are not directly associated with a refinery. "Information is not available on the relative size of basic petrochemical operations by company because these operations are completely integrated with other manufacturing functions."*

The literature consulted for this study did not provide employment data for the separate group of companies or subsidiaries defined as producers of basic petrochemicals from petroleum refining streams. Employment data were found for the larger group of companies defined in SIC Code 2911. The larger group includes the refinery-associated companies but probably does not include the companies not associated with a refinery. In 1974, 94,000 production workers were involved in petroleum refining operations. These operations included production of BTX, solvents, and probably some olefins; but this production was a small percent of the total production of the refining industry. Table 2 shows the total volume of production for the basic petrochemical industry in 1974 by product.

---

* Federal Energy Administration (Office of Economic Impact). Report to Congress on Petrochemicals. Public Law 93-275, Section 23 (no date: circa 1974).

Table 1. OPERATIONS IN THE BASIC PETROCHEMICALS INDUSTRY

Raw Material	Operation	Product or Intermediate Product
Natural gas liquids Refinery gases Naphtha and heavier feedstocks	Olefins Production (Processes 1 - 13)	Ethylene Propylene Mixed C_4 Stream Pyrolysis Gasoline
Mixed C_4 stream from olefins production Refinery gases	Butadiene Production (Processes 14 - 22)	Butadiene Butenes Isobutylene or Polymerized Product
Pyrolysis gasoline from olefins production C_6-C_9 fraction of catalytic reformate	BTX Production (Processes 15 - 23)	Benzene Toluene Mixed C_8 Aromatics Separated C_8 Isomers
Heavy reformate Heavy fraction of pyrolysis gasoline from olefins production Catalytic cycle oil	Naphthalene Production (Processes 24 and 25)	Naphthalene
Caustic extract from treatment of petroleum distillate	Production of Cresols and Cresylic Acids (Processes 26 and 27)	Mixed Cresols Separated Cresol Isomers Cresylic Acid Xylenols Phenol
Naphtha Gas-oil Kerosene	Separation of Normal Paraffins (Process 28)	C_5-C_7 Normal Paraffins C_{10}-C_{15} Normal Paraffins

Table 2. 1974 PRODUCTION OF BASIC PETROCHEMICALS

Material	Production (billion lbs)	Production (Tg, billion kg)
Ethylene	23.52	10.67
Benzene	11.07	5.02
Propylene	9.82	4.45
Toluene	7.49	3.40
Mixed xylenes	5.79	2.63
Butadiene (1,3-)	3.66	1.66
Para-xylene	2.68	1.22
Naphthalene	1.0 - 1.3	0.45 - 0.59
Ortho-xylene	1.05	0.476
Normal paraffins[a]	0.67	0.30
Mixed cresols, cresylic acids	0.197	0.089

[a] 1971 Consumption

Source: Anonymous. "Recession Clamped a Lid on Growth in Chemical Output Last Year, with Production Down for Many Major Producers." Chemical & Engineering News, 53(22) (2 June 1975), 31-34.

Hedley, W. H., et al. Potential Pollutants From Petrochemical Processes. MRC-DA-406. Dayton, Ohio: Monsanto Research Corp., December 1973.

Tables C-10 and C-11 in the Appendix list locations at which basic petrochemicals are manufactured. The tables indicate whether or not the location is directly associated with a refinery and also indicate which basic petrochemicals are produced at the location. Table 3, which summarizes the information in Tables C-10 and C-11 by state, shows that 47 percent of the facilities are located in Texas and Louisiana. Many of the Texas and Louisiana locations are centered in the highly populated Gulf Coast area, but some of the Texas facilities are located in the less highly populated cities of West Texas.

Some interrelated factors which influence change or growth in the basic petrochemicals industry are feedstock availability, capacity, and demand for products from downstream users. World trade and its influence on the import/export situation are also related to growth or change in the industry. Growth or increase in production can be predicted to occur when demand exceeds capacity and domestic production is economically favored over importing.

Significant feedstock changes are anticipated from the industry. Recent petroleum and natural gas shortages have limited petrochemical production. As a result, a shift toward petrochemical production from other fossil fuels and heavier petroleum feedstocks is predicted. The amount of ethylene production from naphtha, crude distillation residuals, and crude will increase. Table 4 shows predicted products from cracking crude oil to produce 500 Gg (one billion pounds) of ethylene per year. Crude oil requirements for ethylene production from crude oil cracking are one-fifth of the crude requirements for the naphtha required to produce the same amount of ethylene. Table 5 shows a predicted product slate for coal based production of petrochemicals. Predictions are that by 1980 all petrochemical feedstock demand could be supplied by processing 0.5 Tg (500,000 tons) of coal per day.

The years 1974 and 1975 were generally a time of shortages in capacity for the industry. Increases in capacity require massive capital investments and three- to five-year lead times. Such increases are anticipated to occur mainly through alterations in industry structure through forward integration of the oil companies and backward integration of the chemical companies. Petroleum refiners are expected to invest in chemical production in an attempt to increase profits, since chemical operations provide better profits than other oil company operations. It is predicted that oil companies will gain a share of the market in downstream large volume intermediates such as phenol, ethylene oxide, polyethylene, styrene, and vinyl chloride. Table 6 summarizes published predictions of future demand and projected growth rates for some of the basic petrochemicals.

Table 3. GEOGRAPHIC LOCATION OF BASIC PETROCHEMICAL MANUFACTURING FACILITIES

State or Location	Number of Facilities	Percent of Total
Texas	38	36
Louisiana	12	11
Illinois	9	8
California	7	7
New Jersey	6	6
Puerto Rico	5	5
Kentucky	4	4
Ohio	4	4
Pennsylvania	3	3
Delaware	3	3
Michigan	2	2
Oklahoma	2	2
Indiana	2	2
Kansas	2	2
Arkansas	2	2
Six* other locations	1 each	6

* Alabama, Iowa, Mississippi, New York, Virginia, Virgin Islands

Table 4. PRODUCTS FROM CRUDE OIL CRACKING TO PRODUCE 500 Gg (ONE BILLION POUNDS) ETHYLENE PER YEAR

Product	Quantity Gg/yr	Quantity 10^6 lb/yr
Ethylene	500	1,000
Acetylene	90	200
Propylene	60	135
Crude butadiene	40	90
Crude BTX	200	435
By-product fuel		Sufficient quantity to supply the ethylene plant

Source: Ponder, T. C. "Petrochemicals--More for 1974." Hydrocarbon Processing, 53 (May 1974), 81-83.

Table 5. EXAMPLE PRODUCT SLATE FROM COAL UTILIZATION FOR PETROCHEMICAL FEEDSTOCKS

Product	Approximate Percent By Weight
C_1-C_4 hydrocarbons	30
Fuel oil	16
Naphtha	3
BTX	33
Char, H_2S, NH_3, H_2O	18

Source: Ponder, T. C. "Petrochemicals--More for 1974." Hydrocarbon Processing, 53 (May 1974), 81-83.

Table 6. 1974 PREDICTIONS FOR FUTURE DEMAND AND GROWTH RATE OF BASIC PETROCHEMICALS

Basic Petrochemical	Predicted Demand	Year	Predicted Annual Growth Rate
Ethylene	16.8 Tg (18.5×10^6 tons) capacity 15.4 Tg (17×10^6 tons) consumption	1980	7.5% (ethylene production) 8.5% (ethylene feedstocks)
Naphthalene	7.57 dm^3 (2×10^6 gallons)	1980	Expect demand to decrease due to replacement by ortho-xylene in phthalic anhydride production
Butadiene			4.2 percent
Benzene	7.199 hm^3 (1902×10^6 gallons)	1980	Worldwide demand will increase 10% per year
Toluene	1.21 hm^3 (319×10^6 gallons)	1980	
Xylenes	3.34 hm^3 (882×10^6 gallons)	1980	

Source: Ponder, T. C. "Petrochemicals--More for 1974." Hydrocarbon Processing, 53 (May 1974), 81-83.

Table 7. 1973 FEEDSTOCK REQUIREMENTS OF THE BASIC PETROCHEMICALS INDUSTRY

Raw Material and Description	Total Volume Consumed or Produced	Volume Utilized For Basic Petrochemical Production	Remarks
Natural Gas (Methane)	623 km^3 (22 x 10^{12} ft^3) (not including gas liquids and other hydrocarbons)	22.7 km^3 (800 x 10^9 ft^3) (3.6% of total consumption)	Used for ammonia and methanol manufacture. Also used for steam and power generation and plant fuel.
Ethane from natural gas (less than 10 percent is obtained from refineries)	Most recovered ethane is used for petrochemical feedstock. Total ethane consumption contained energy equivalent to 1.5 percent of the energy of natural gas consumed in U.S.		Half of ethylene production was based on ethane
C_3 and C_4 Hydrocarbons including propane, n-butane, isobutane, propylene, and butylene from natural gas processing plants and refineries	53.9 hm^3 (339 x 10^6 barrels) of propane (63%), n-butane (27%), and isobutane (10%) recovered in 1973. 55-60 hm^3 (350-400 x 10^6 barrels) C_3 and C_4 hydrocarbons produced in refineries by cracking and reforming.	20.7 hm^3 (130 x 10^6 barrels) or 20 percent of production	----
Naphtha (gasoline boiling range hydrocarbons) including field condensate and raffinates Reformate	416 hm^3 (2,620 x 10^6 barrels) were consumed	10 hm^3 (70 x 10^6 barrels) or 2.7 percent of consumption. 8.27 x hm^3 (52 x 10^6 barrels) of reformate were used for aromatics.	Governed by allocations
Heavy fractions Kerosene	60.4 hm^3 (380 x 10^6 barrels) of kerosene used for jet and other fuel	0.3 hm^3 (2 x 10^6 barrels) of normal paraffins extracted from kerosene in 1973.	----
Gas-Oil	----	4.3 hm^3 (27 x 10^6 barrels) were used for olefin production or about one percent of the distillate oils produced from crude.	----

SOURCE: Federal Energy Administration (Office of Economic Impact). Report to Congress on Petrochemicals. Public Law 93-275, Section 23, (no date: circa 1974).

Raw Materials

"The petrochemical industry is dependent upon the natural gas and petroleum refining industries for its feedstock. In 1973, estimated petrochemical feedstock usage of natural gas was about 800 billion cubic feet, or 3.6 percent of total consumption. Natural gas liquids and refinery fraction consumption was about 330 million barrels, or 5.1 percent of 1973 demand. The energy content of petroleum and natural gas hydrocarbons consumed as petrochemical feedstocks was about 4 percent of the total energy from these sources."* Table 7 summarizes volumes of each raw material consumed by the basic petrochemical industry in 1973. The U.S. government exercises price and allocation controls on the feedstocks employed by this industry.

In general, basic petrochemical plants can be characterized on the basis of their location with respect to a refinery and their feedstocks. Some plants are refinery connected. These are located at or near refineries; they isolate ethylene from refinery off-gases and they use other refinery products (ethane reformate, or naphtha) for at least part of their feedstock. Others use feedstocks obtained from natural gas processing or oil field condensate plants.

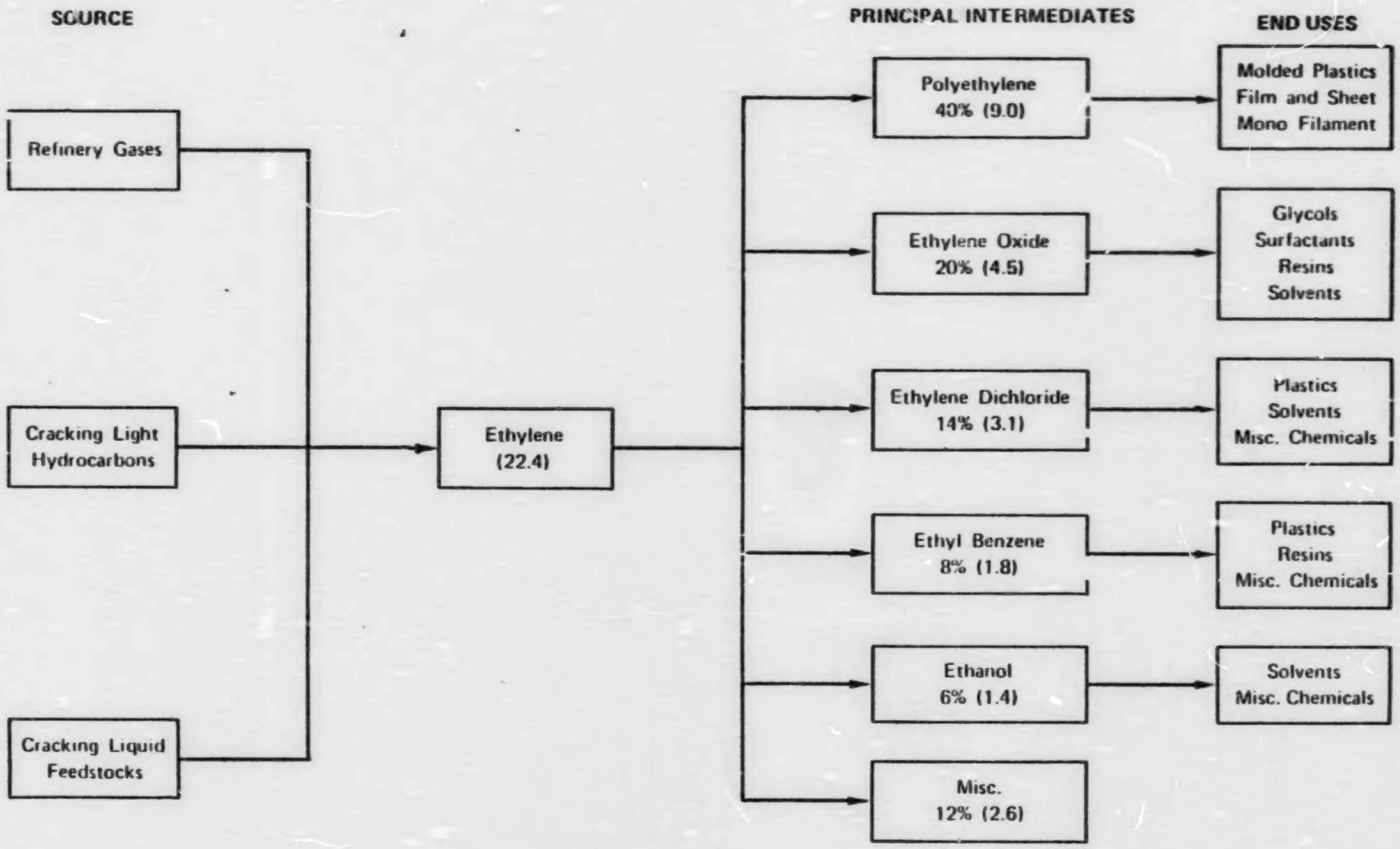
Products

The basic petrochemicals industry produces solvents and chemicals of various grades or specifications which are used to produce industrial organic chemicals. For some of the basic petrochemicals only a portion of the production is diverted to petrochemical use. A large portion of the production of aromatics and other petrochemicals is returned to the refinery for use in gasoline and aviation fuels.

Approximately 2500 organic chemical products are produced directly or indirectly from basic petrochemicals. The industrial organic chemicals produced from basic petrochemicals are employed in downstream industries including plastics and resins, synthetic fibers, elastomers (synthetic rubber), plasticizers, explosives, surface active agents, dyes, surface coatings, pharmaceuticals, and pesticides. Figures 1 through 4 show the major industrial organic chemicals produced from ethylene, propylene, benzene and butadiene. Toluene is used as a high octane gasoline component, to produce benzene, and in the production of plastics, dyes, solvents, explosives and specialty chemicals. Only a small portion of the C_8 aromatics (mixed xylene) production is used for chemical production. Ortho- and para-xylene are the isomers used most widely for chemical intermediates. Ortho-xylene is used to produce phthalic anhydride, and para-xylene is used to produce

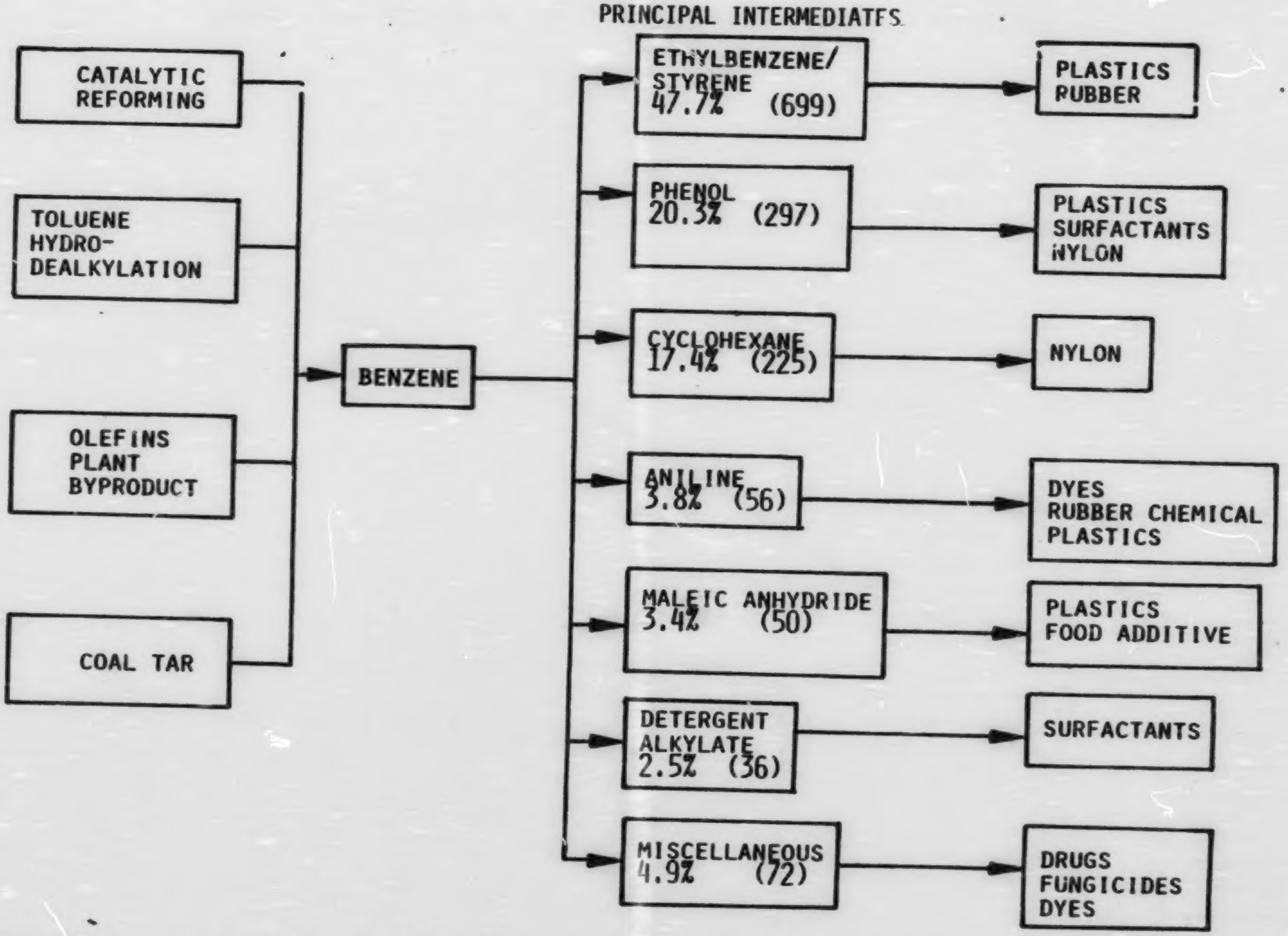
---

* Federal Energy Administration (Office of Economic Impact). Report to Congress on Petrochemicals. Public Law 93-275, Section 23, (no date: circa 1974).


SOURCE
PRINCIPAL INTERMEDIATES
END USES
Refinery Gases
Cracking Light Hydrocarbons
Cracking Liquid Feedstocks
Ethylene (22.4)
Polyethylene 40% (9.0)
Ethylene Oxide 20% (4.5)
Ethylene Dichloride 14% (3.1)
Ethyl Benzene 8% (1.8)
Ethanol 6% (1.4)
Misc. 12% (2.6)
Molded Plastics Film and Sheet Mono Filament
Glycols Surfactants Resins Solvents
Plastics Solvents Misc. Chemicals
Plastics Resins Misc. Chemicals
Solvents Misc. Chemicals

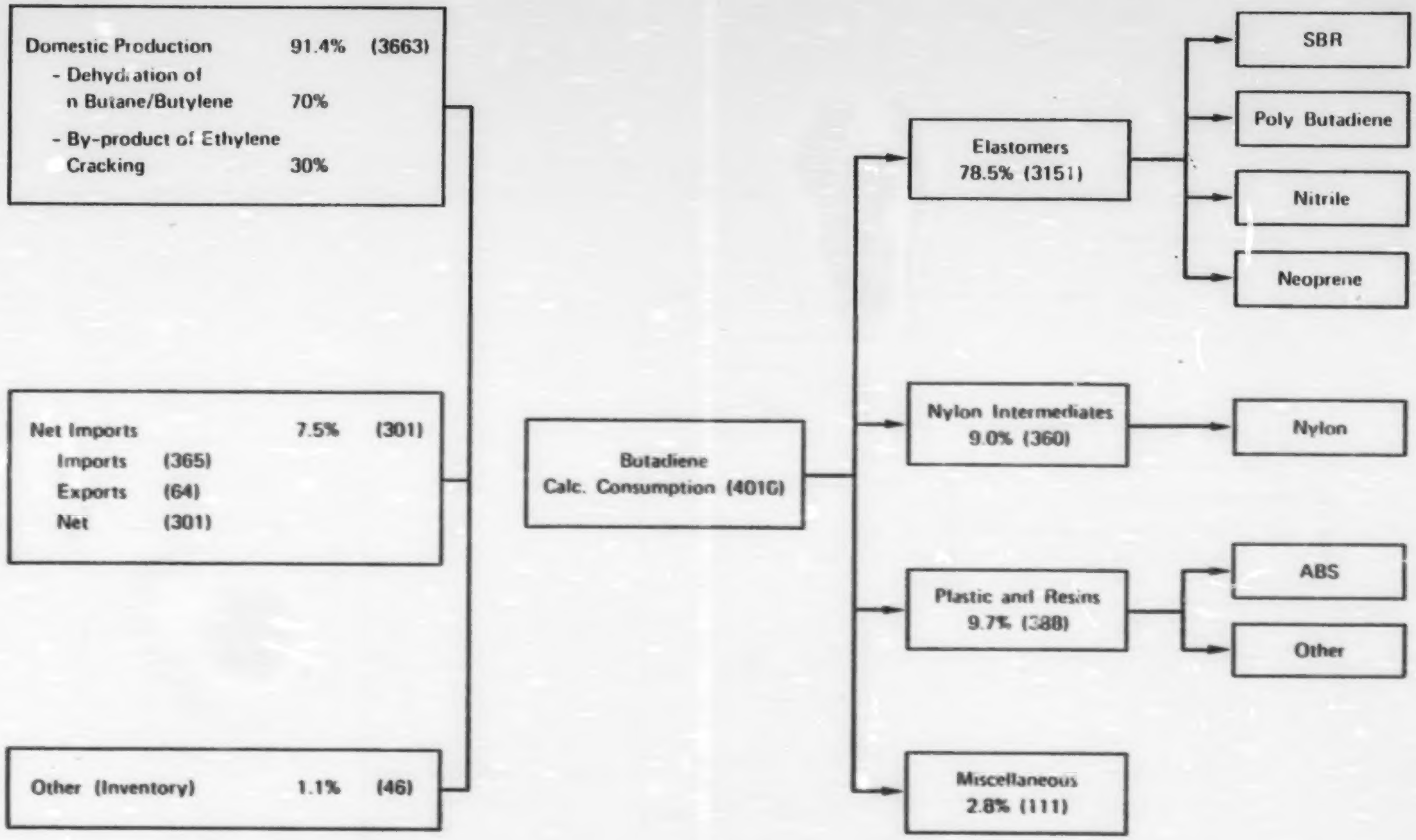
Source: Federal Energy Administration (Office of Economic Impact). Report to Congress on Petrochemicals. Public Law 93-275, Section 23, (no date: circa 1974).

Figure 1. PETROCHEMICAL USE OF ETHYLENE IN 1973 (BILLION POUNDS)


PRINCIPAL INTERMEDIATES
CATALYTIC REFORMING
TOLUENE HYDRO-DEALKYLATION
OLEFINS PLANT BYPRODUCT
COAL TAR
BENZENE
ETHYLBENZENE/ STYRENE 47.7% (699)
PHENOL 20.3% (297)
CYCLOHEXANE 17.4% (225)
ANILINE 3.8% (56)
MALEIC ANHYDRIDE 3.4% (50)
DETERGENT ALKYLATE 2.5% (36)
MISCELLANEOUS 4.9% (72)
PLASTICS RUBBER
PLASTICS SURFACTANTS NYLON
NYLON
DYES RUBBER CHEMICAL PLASTICS
PLASTICS FOOD ADDITIVE
SURFACTANTS
DRUGS FUNGICIDES DYES

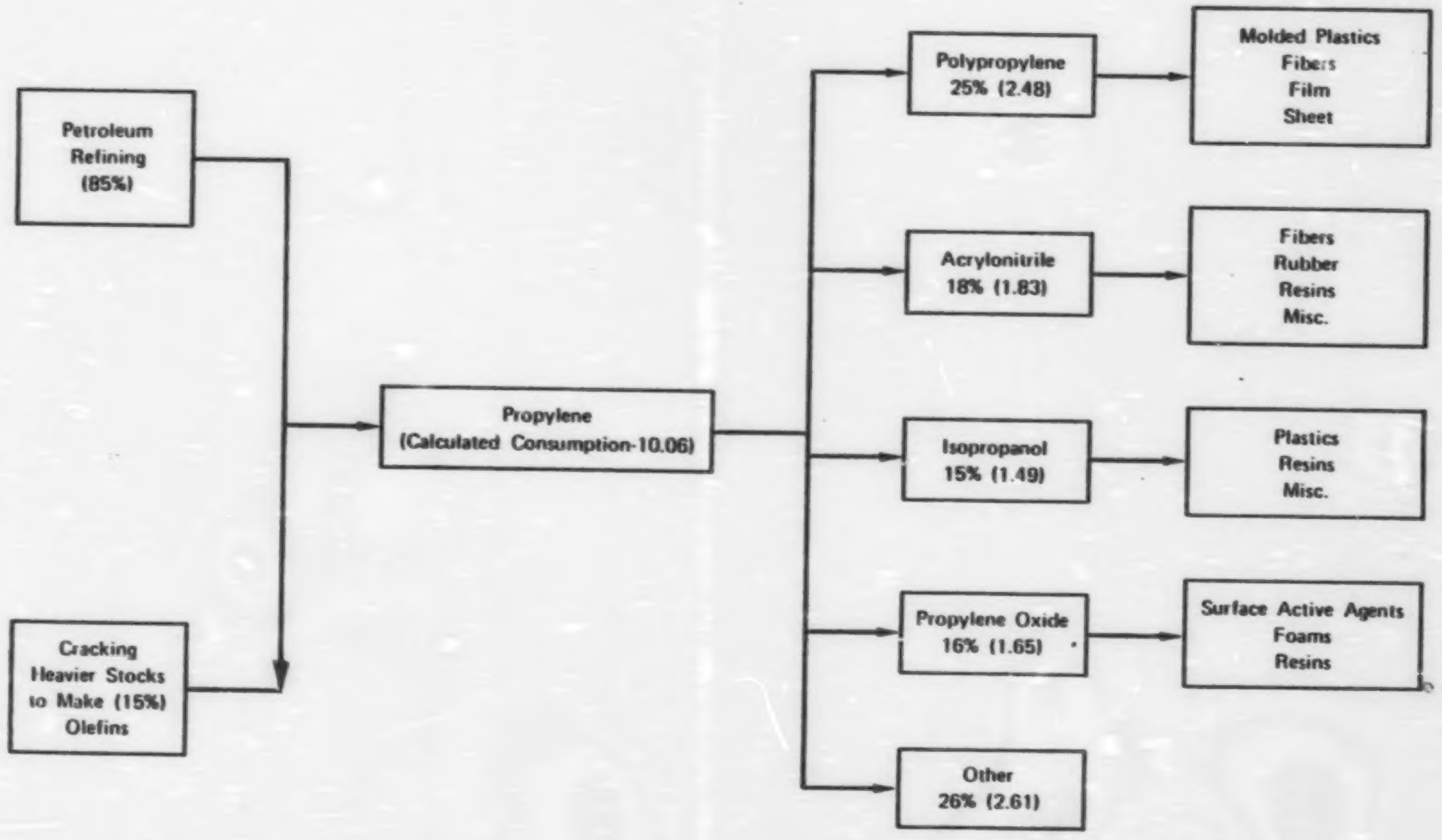
Source: Federal Energy Administration (Office of Economic Impact). Report to Congress on Petrochemicals. Public Law 93-275, Section 23, (no date: circa 1974).

Figure 2. PETROCHEMICAL USE OF BENZENE IN 1973 (MILLION GALLONS)


Domestic Production 91.4% (3663)
- Dehydration of n Butane/Butylene 70%
- By-product of Ethylene Cracking 30%
Net Imports 7.5% (301)
Imports (365)
Exports (64)
Net (301)
Other (Inventory) 1.1% (46)
Butadiene
Calc. Consumption (4010)
Elastomers
78.5% (3151)
Nylon Intermediates
9.0% (360)
Plastic and Resins
9.7% (388)
Miscellaneous
2.8% (111)
SBR
Poly Butadiene
Nitrile
Neoprene
Nylon
ABS
Other

Source: Federal Energy Administration (Office of Economic Impact). Report to Congress on Petrochemicals. Public Law 93-275, Section 23, (no date: circa 1974).

Figure 3. PETROCHEMICAL USE OF BUTADIENE IN 1973 (MILLION POUNDS)


Petroleum Refining (85%)
Cracking Heavier Stocks to Make (15%) Olefins
Propylene (Calculated Consumption-10.06)
Polypropylene 25% (2.48)
Acrylonitrile 18% (1.83)
Isopropanol 15% (1.49)
Propylene Oxide 16% (1.65)
Other 26% (2.61)
Molded Plastics Fibers Film Sheet
Fibers Rubber Resins Misc.
Plastics Resins Misc.
Surface Active Agents Foams Resins

Source: Federal Energy Administration (Office of Economic Impact). Report to Congress on Petrochemicals. Public Law 93-275, Section 23, (no date: circa 1974).

Figure 4. PETROCHEMICAL USE OF PROPYLENE IN 1973 (BILLION POUNDS)

terephthalic acid and dimethyl terephthalate. These chemicals are used in the plasticizers and synthetic fibers industries. Seventy-five percent of the naphthalene produced is used in phthalic anhydride manufacture. Normal paraffins in the C_5-C_7 range are used as specialty solvents. while those in the C_{10}-C_{15} range are used in the production of linear alkylbenzene sulfonates for biodegradable detergents. The largest use for cresols and cresylic acids is for phosphate esters.

Table B-1 in the Appendix lists products and by-products of the basic petrochemicals industry. The limited resources available for this study did not permit the inclusion of information describing the grades and specifications available for each chemical or mixture. Since the basic petrochemicals serve either as raw materials for downstream organic products or as precursors to intermediates for downstream organic products, their purity is critical and is usually determined by the most demanding end use. They are produced in purities ranging from 90+% to 99.99+%. The maximum impurities allowed are from 0.5 to 5000 ppm depending on the impurity and ultimate end use.

Companies

The majority of the output from the basic petrochemicals industry is produced by petrochemical divisions or subsidiaries of major oil companies as indicated in Table 8. While these are legal subdivisions of oil companies and probably separate entities for accounting purposes, they are actually a part of the oil companies. Since the petrochemical plants are dependent on refineries, gas processing plants, or field condensate plants for their raw materials, they are located near the petroleum processing sites to facilitate stream transfers. In some cases they are actually located within the same fence.

Table 8. BASIC PETROCHEMICAL PRODUCTION BY PETROLEUM REFINERS IN 1974

	Percent of 1974 Capacity		
Basic Petrochemical	Petroleum Refiners	Chemical Companies	Other
Benzene	70	17	13
Ethylene	40	45	15
Chemical Grade Propylene	>60		

Source: Greek, Bruce F. "Chemicals Again Lure the Oil Industry." Chemical & Engineering News, 53(50) (15 December 1975), 12-14.

Large, multiline chemical companies also produce a portion of the basic petrochemicals. As is the case for major oil companies, there is a significant incidence of vertical integration in the chemical companies which produce basic petrochemicals.

The data utilized for this study did not readily indicate the existence of a significant population of independent companies that purchase natural gas processing or refinery products, produce basic petrochemicals, then sell them to distinctly separate companies that use them to produce industrial organic chemical intermediates. It is possible that some of the companies in Table C-11 (Appendix C), such as Petro-Tex Chemical Corporation, are classified in this category.

There are other companies that also produce a small volume of the aromatic chemicals produced by this industry. These companies use primarily coal-derived rather than petroleum-derived raw materials, and the operations (groups of processes) employed are somewhat different than those employed by the basic petrochemical industry. Some petroleum-based petrochemical plants have facilities for treating purchased coke oven light oil or coal tar distillates. In general, however, production of chemicals from coal is accomplished by a separate population of companies. The published production data for some products in Table 1 may include production from coal-derived raw materials. This portion of the production is generally small. An attempt was made to exclude companies utilizing coal-derived raw materials from the company/product lists in Appendix C.

Table 9 lists companies which have the major capacities for each basic petrochemical. Sources of data and inconsistencies in data are described in the footnotes to the table.

Environmental Impact

In general the waste streams from this industry are quite similar to those of the petroleum refining industry. The industry employs processes which separate hydrocarbon mixtures into pure components and byproduct hydrocarbons. To avoid discarding valuable hydrocarbon streams, the byproducts are used for fuel or are converted to other refinery products. Estimated hydrocarbon emissions are in the range from 0.1 to 0.6 percent of plant throughput. Hydrocarbons are emitted in low concentrations in wastewater, as fugitive gaseous emissions, and in solid residues. Some of the hydrocarbons emitted are photochemically reactive. Other non-hydrocarbon pollutants emitted are water treatment wastes including fouling and corrosion inhibitors, products from sulfur and nitrogen removal processes, spent catalysts and solid adsorbents, combustion and incineration products, and wastes from catalyst cleaning operations.

Auxillary processes are employed by the basic petrochemical industry for process heating (steam or fired heaters) and cooling (cooling water or refrigeration). Operation of the steam generation and cooling water systems produces the major portion of wastewater from the industry. Emissions from fired heaters are described in Chapter 3, The Petroleum Refining Industry. Electric power is usually purchased by this industry rather than produced on-site.

Table 9. LARGE VOLUME PETROCHEMICAL PRODUCERS[a,b,c]

Products and Companies	Capacity (10^6 lb/yr)[d]	Gg	Percentage of Total	Remarks
Cresols and Cresylic Acids (Recovered from Petroleum)				
Merichem Co.	100	45	Assumed 100%	Some synthetic production included. 1973 Data
Northwest Petroleum	15	7		
Pitt-Consol	50	20		
Productol Chem. Co.	30	10		
Butadiene				
Atlantic Richfield Co.	280	130	78%	1975 Data
El Paso Natural Gas Co.	200	90		
Exxon Chemical Co., USA	340	150		
Firestone Tire & Rubber Co.	220	100		
Neches Butane Products	640	290		
Petro-Tex Chemical Corp.	990	450		
Phillips Petroleum Co.	290	130		
Puerto Rico Olefins Co.	200	90		
Shell Chemical Co.	265	120		
Mixed Xylenes (from Petroleum)				
Atlantic Richfield Co.	430	200	78%	1971 Data
Cities Service Co., Inc.	520	240		
Commonwealth Oil Refining Co.	570	260		
Phillips Petroleum Co.	720	330		
Shell Oil Company	505	230		
Standard Oil of California	980	440		
Standard Oil Co. (Indiana)	1075	488		
Standard Oil Co. (New Jersey)	860	390		
Sun Oil Company	465	211		
Tenneco, Inc.	360	160		
Toluene (from Petroleum)				
Amerada Hess Corp.	290	130	68%	1972 Data
Ashland Oil, Inc.	360	160		
Atlantic Richfield Co.	420	190		
Mobil Oil Corp.	500	200		
Monsanto Co.	325	148		
Phillips Petroleum Co.	650	300		
Shell Oil Co.	360	160		
Standard Oil Co. (Indiana)	1150	522		
Standard Oil Co. (New Jersey)	940	430		
Sun Oil Co.	530	240		
Propylene				
Amoco Chemicals Corp.	1090	490	66%	All Grades. 1975 Data
Atlantic Richfield Co.	505	230		
Chevron Chemical Co.	740	340		
Dow Chemical USA	910	410		
Exxon Chemical Co., USA	1990	903		
Gulf Oil Corp.	495	225		
Shell Oil Co.	1170	531		
Sun Oil Co.	450	200		
Union Carbide Co.	1285	583		

Table 9. LARGE VOLUME PETROCHEMICAL PRODUCERS[a,b,c] (Cont.)

Products and Companies	Capacity (10^6 lb/yr)[d]	Gg	Percentage of Total	Remarks
Naphthalene (from Petroleum)				
Ashland Oil, Inc.	100	45	Not Available	1974 Data
Getty Oil Co.	100	45		
Kewanee Oil Co.	Not Available			
Monsanto Co.	100	45		
Sun Oil Co.	150	68		
n-Paraffins				
Continental Oil Co.	225	102	Assumed 100%	1974 Data. C_{10}-C_{15} Range
Exxon Corp.	220	100		
Shell Chemical Co.	100	45		
South Hampton Co.	60	30		
Union Carbide Corp.	240	110		
Ethylene				
Cities Service Co., Inc.	940	430	67%	1974 Data
Dow Chemical, USA	3770	1710		
Exxon Chemical Co., USA	1770	804		
Gulf Oil Chemicals Co.	1570	710		
Phillips Petroleum Co.	1140	518		
Shell Oil Co.	2050	930		
Union Carbide Corp.	4315	1959		
Benzene				
Atlantic Richfield Co.	625	284	68%	1975 Data
Coastal States Gas Corp.	515	234		
Commonwealth Oil Refining Co.	1360	617		
Dow Chemical USA	515	234		
Exxon Corp.	985	447		
Gulf Oil Corp.	1045	474		
Monsanto Co.	550	250		
Phillips Petroleum Co.	970	440		
Shell Chemical Co.	1030	470		
Standard Oil Co. (Indiana)	625	284		
Sun Oil Co.	510	230		
Tenneco, Inc.	660	300		

---

[a] Production of subsidiaries may be listed with parent company's capacity.

[b] Butylenes are generally used captively. Their production capacity is hard to determine.

[c] Information provided by Monsanto Research Corporation, Directory of Chemical Producers, 1975, and Chemical Marketing Reporter, 18 Feb., 1974. Details are summarized in Tables C-1 through C-9. Data therein may be inconsistent with data in Tables C-10 and C-11.

[d] Estimates assumed accurate to the nearest 5×10^6 lbs. Conversions made to the same number of significant figures or to the nearest Gg.

Wastewater, which is the major source of emissions from the basic petrochemical industry, has been described in five categories:

(1) Wastes containing a principal raw material or product;

(2) By-products produced during reactions;

(3) Spills, leaks, washdowns, vessel cleanouts, or point overflows;

(4) Cooling tower and boiler blowdown, steam condensate, water treatment wastes, and general washing water; and

(5) Surface runoff.

For purposes of developing wastewater emission control guidelines for the industry, basic petrochemical production processes have been categorized according to modes of water use. The categories and some examples are listed as follows:

Non-aqueous processes: Hydrotreatment of pyrolysis gasoline, solvent extraction of BTX from reformate, C_8 aromatics isomerization and crystallization.

Processes with water contact as steam diluent or absorbent: Production of ethylene and propylene by pyrolysis, butadiene production by dehydrogenation.

Aqueous liquid phase reactions: Isobutylene extraction with sulfuric acid.

Solids disposal is a significant problem for the industry. The waste solids occur in diverse forms. Nearly every plant has some form of solid waste disposal or handling facility on site. The general methods of disposal are: land disposal, incineration, salvage and recycle, and chemical and biological treatment. In some cases ocean disposal is permitted. The solids are composed of water treatment sludge; ashes, flyash and incinerator residue; plastics; ferrous and nonferrous metals including catalysts; organic chemicals; inorganic chemicals; filter cakes; and viscous solids.

Gaseous emissions are minor in comparison to the solids and wastewater. The major air pollutants are particulates and hydrocarbons. Particulates are vented to the air during steam-air decoking. Hydrocarbons may be emitted to the atmosphere through fugitive losses or as vent gases from process operations. Large quantities of hydrocarbon containing gases may be emitted during upset conditions by passage through safety valves, usually to a flare for disposal. Some emissions of SO_x, NO_x, and carbon monoxide occur from pyrolysis facilities, decoking, or fired heaters. In general there are few processes that emit large volume waste gas streams to the atmosphere.

Data on volumes and compositions of emissions to air, land, and water from the industry as defined herein were unavailable. Waste streams from particular processes were identified either from descriptions in the literature or by predictions based on knowledge of the process. Plant wastes result from a combination of waste streams from particular processes. Waste management operations and facilities are probably of the same degree of sophistication as those of the petroleum refining industry. Ethylene plant emissions are an exception in that they are well described. Data are given in the section on Olefins Production.

Bibliography

(1) Anonymous. "Recession Clamped a Lid on Growth in Chemical Output Last Year, with Production Down for Many Major Producers." Chemical & Engineering News, 53(22) (2 June 1975), 31-34.

(2) Catalytic, Inc. Capabilities and Costs of Technology for the Organic Chemical Industry to Achieve the Effluent Limitations of P. L. 92-500. Final Report, PB 244 544. Philadelphia, Pennsylvania, June 1975.

(3) Clancy, G. M. Radian Corporation, personal communication (March 1976).

(4) DeWitt, J. D. "Olefins Outlook." Hydrocarbon Processing, 53 (November 1974), 121-128.

(5) Erskine, Mimi G. "Benzene," 618.5021 A. Chemical Economics Handbook. Menlo Park, California: Stanford Research Institute, 1972.

(6) Environmental Protection Agency (Office of Water and Hazardous Materials, Effluent Guidelines Div.). Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category. EPA 440/1-74-009-a. Washington, D. C.: 1974.

(7) Federal Energy Administration (Office of Economic Impact). Report to Congress on Petrochemicals. Public Law 93-275, Section 23, (no date: circa 1974).

(8) Garner, D. N. Radian Corporation, personal communication regarding work done on EPA Contract 68-02-1319, Task 51 (March 1976).

(9) Greek, Bruce F. "Chemicals Again Lure the Oil Industry." Chemical & Engineering News, 53(50) (15 December 1975), 12-14.

(10) Gloyna, E. F. and D. L. Ford. "The Characteristics and Pollutional Problems Associated with Petrochemical Wastes." Prepared for FWPCA Contract 14-12-461, Ada, Oklahoma: Robert S. Kerr Water Research Center, February 1970.

(11) Hahn, A., A. Chaptal and J. Sialelli. "Why Olefin Specs Have Changed." Hydrocarbon Processing, 54 (February 1975), 89-92.

(12) Hedley, W. H., et al. Potential Pollutants From Petrochemical Processes. MRC-DA-406. Dayton, Ohio: Monsanto Research Corp., December 1973.

(13) Kent, James A., ed. Riegel's Handbook of Industrial Chemistry. 7th ed. N.Y.: Van Nostrand Reinhold Company, 1974.

(14) Mencher, S. K. "Minimizing Waste in the Petrochemical Industry." Chemical Engineering Progress, 63 (October 1967) 80-88.

(15) Ockerbloom, N. E. "World Benzene Outlook." Hydrocarbon Processing, 51 (November 1972), 117-124.

(16) Ponder, T. C. "Petrochemicals--More for 1974." Hydrocarbon Processing, 53 (May 1974), 81-83.

(17) Sittig, Marshall. Pollution Control in the Organic Chemical Industry. Park Ridge, N.J.: Noyes Data Corporation, 1974.

(18) Stanford Research Institute. Chemical Economics Handbook. Menlo Park California.

(19) Stanford Research Institute. 1975 Directory of Chemical Producers, U.S.A. Menlo Park, California: 1975.

(20) U. S. Bureau of the Census. Statistical Abstract of the United States: 1975. 96th edition. Washington, D. C.: 1975.

(21) "Xylene Output Seen Doubling." Chemical Marketing Reporter. (16 February 1975), 7.

(22) Zdonik, S. B., E. J. Bassler and L. P. Hallee. "How Feedstocks Affect Ethylene." Hydrocarbon Processing, 53 (February 1974), 73-75.

INDUSTRY ANALYSIS

The basic petrochemicals industry is described by six operations composed of related processes. Process descriptions and operations are somewhat generalized in an effort to accomodate the many variations in modes of processing that exist due to site-specific and economic factors. This was a desk-top study of a very complex industry, and the prescribed brevity of process descriptions has resulted in some oversimplification.

Each operation is described by a flow sheet indicating input materials (brackets), processes (numbered rectangles), and product and by-product streams (large circles). Solid, liquid, and gaseous waste streams are indicated by the small squares, triangles and circles, respectively, attached to the numbered process rectangles. Process descriptions follow the flow sheets on which they are presented.

Data are given in metric units according to the System Internationale described in the ASTM Metric Practice Guide. Preferred base units and rules for rounding numbers converted from one system of units to another are described therein.

The information used to prepare this catalog entry consisted of books, encyclopedias, results of EPA supported investigations, consultations with industry experts in olefin manufacture and refinery-associated petrochemical operations, and several recently published trade journal articles. There are additional sources of information such as the open literature, patent literature, and publications of Stanford Research Institute's Process Economics Program which were not utilized because of the limited resources available for this study. The reader is advised to consult these additional sources of information on subjects which were not treated in depth.

There are some recognized deficiencies and inconsistencies in the data used to prepare this report. Since the data were originally collected for other purposes, they were not entirely suitable. For example, there are reporting problems in Tariff Commission data on chemicals with both petrochemical and fuel uses. As a result, utilization of natural gas liquids and refinery products for consumption by basic petrochemical producers is not accurately known.

OLEFINS PRODUCTION PROCESSES

The Olefins Production Operation of the Basic Petrochemical Industry is based on what is commonly called an ethylene plant. Because of the current demand for ethylene, the olefins plants are usually operated for maximum ethylene production, although propylene, C_4 compounds, fuel oil, pyrolysis gasoline, methane, and hydrogen are also produced. The hydrogen and fuel oil are commonly used captively; the propylene and ethylene are marketed as products; the C_4 compounds may be marketed or further processed in the Butadiene operation; and the pyrolysis gasoline is further processed in the BTX Production operation

The product-to-by-product ratios are dependent upon feedstock as well as on mode of operation. Common feedstocks for this operation include natural gas liquids (ethane, propane, butane), refinery gases, naphtha, and gas-oil. The heavier feedstocks (naphtha and gas-oil) and the refinery gases generally produce more by-products.

Data for utilities for each separate process in this operation are generally unavailable. Some data for an ethylene plant in its entirety are available and are presented in Table 10.

Table 10. UTILITY REQUIREMENTS FOR AN ETHYLENE PLANT [a,b]

Fuel	14 GJ (13.0 x 10^6 Btu)
Cooling Water	130 m^3 (35,000 gal)
Electrical Power	17 kWh
Boiler Feedwater	180 kg (400 lb)

[a] Data are for high severity cracking with ethane recycle. No air-fin cooling is assumed.

[b] Per 1000 lb ethylene. 1 lb = 454g

Source: Chemical Engineering, ed. Sources and Production Economics of Chemical Products, 1973-1974. 1st ed. N.Y.: McGraw Hill, 1974.

Figure 5 is a flowsheet of the processing configuration presented here. The processing sequence presented in this operation is considered to be a typical thermal cracking process utilizing a tubular furnace. Other cracking systems (pebble-bed heaters and fluidized-bed crackers) contribute very little to the total ethylene production. The plant configuration presented is characteristic of the industry. Processing sequences of specific plants may differ somewhat due to locations, marketing factors, and feedstock availabilities. The processes treated in this operation are 1) Thermal Cracking, 2) Oil Quenching, 3) Water Quenching, 4) Compression, 5) Acid Gas Removal, 6) Water Removal, 7) Demethanation, 8) C_2 Separation, 9) C_3 Separation, 10) C_4 Separation, and 11) Heavy Fractionation.

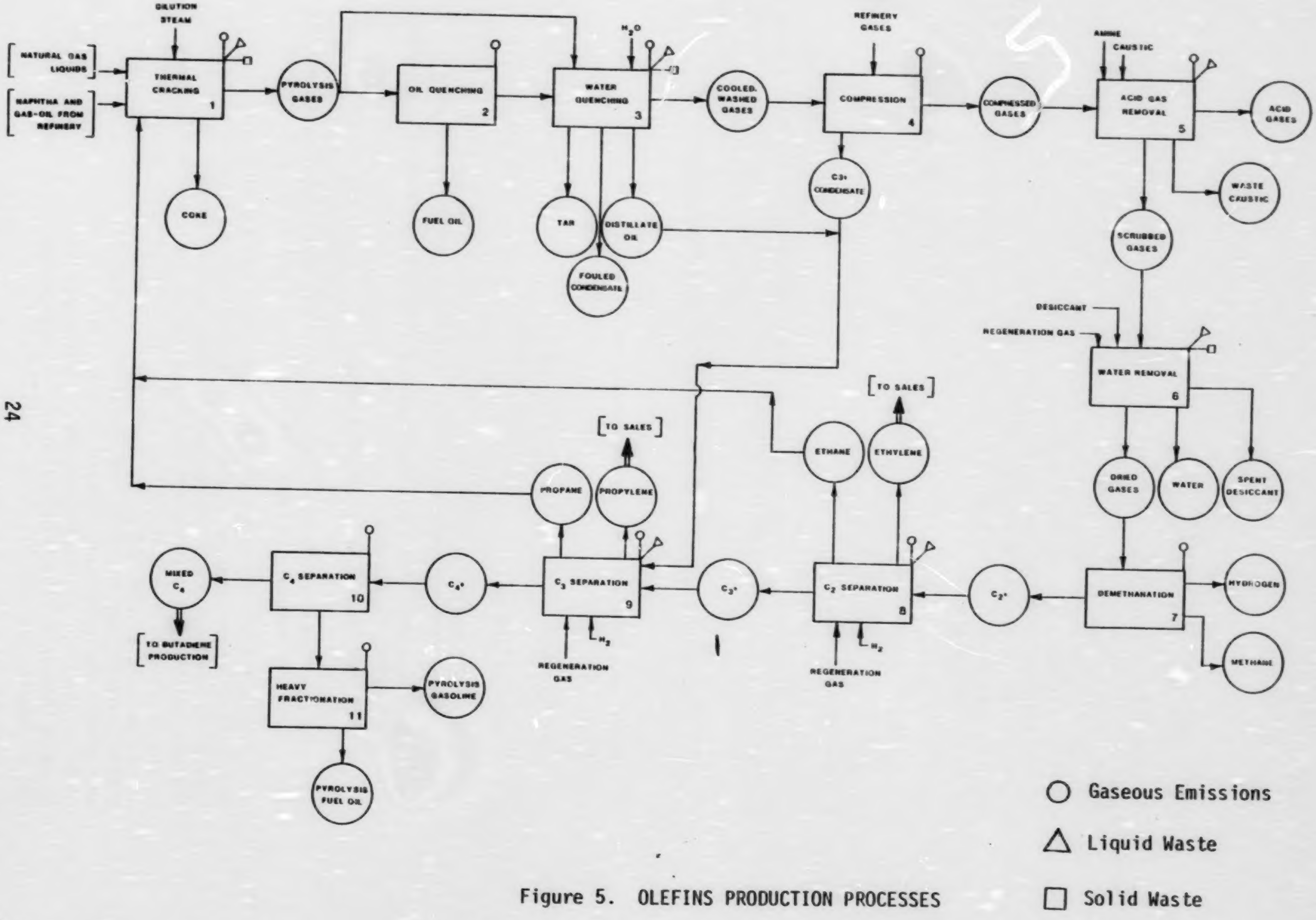

NATURAL GAS LIQUIDS
NAPHTHA AND GAS-OIL FROM REFINERY
DILUTION STEAM
THERMAL CRACKING 1
COKE
PYROLYSIS GASES
OIL QUENCHING 2
FUEL OIL
H_2O
WATER QUENCHING 3
TAR
DISTILLATE OIL
FOULED CONDENSATE
COOLED, WASHED GASES
REFINERY GASES
COMPRESSION 4
C3+ CONDENSATE
COMPRESSED GASES
AMINE
CAUSTIC
ACID GAS REMOVAL 5
ACID GASES
WASTE CAUSTIC
SCRUBBED GASES
DESICCANT
REGENERATION GAS
WATER REMOVAL 6
DRIED GASES
WATER
SPENT DESICCANT
DEMETHANATION 7
HYDROGEN
METHANE
C_2^+
C_2 SEPARATION 8
REGENERATION GAS
H_2
ETHANE
ETHYLENE
TO SALES
C_3^+
C_3 SEPARATION 9
REGENERATION GAS
H_2
PROPANE
PROPYLENE
TO SALES
C_4^+
C_4 SEPARATION 10
MIXED C_4
TO BUTADIENE PRODUCTION
HEAVY FRACTIONATION 11
PYROLYSIS GASOLINE
PYROLYSIS FUEL OIL
○ Gaseous Emissions
△ Liquid Waste
□ Solid Waste

Figure 5. OLEFINS PRODUCTION PROCESSES

Information concerning emissions from the entire ethylene plant is also available; whereas, waste stream information for the separate processes is sparse. The characterization of waste streams from the entire plant is often a useful tool in understanding the emissions problems of the industry. Therefore, the emissions data for the entire plant are presented here. Hydrocarbon losses from a 227 Gg/yr (500 million lb/yr) ethylene plant have been estimated based on emission factors for leaks from valves and seals and fugitive gaseous emissions from storage vessels and liquid waste streams. Estimates prepared using emission factors for a plant employing extensive control measures are summarized in Table II. Fugitive emissions for such a plant are less than one percent of throughput.

Table 11. ESTIMATED HYDROCARBON LOSSES FROM AN ETHYLENE PLANT PRODUCING 227 Gg (500 MILLION LB)/YR[a]

Source	Loss Factor		Estimated Emissions kg/day	(lb/day)
Valves	68g	(0.15 lb)/day/valve	306	675
Pumps (mechanical seals)	1.5 kg	(3.2 lb)/day/seal	218	480
Compressors (centrifugal, mechanical seal)	1.5 kg	(3.2 lb)/day/seal	29	64
Compressors (reciprocal, packed seal)	2.5 kg	(5.4 lb)/day/seal	2	5
Cooling Water	0.7 kg/1000 m^3	(60 lb/10^6 gal)	195	430
Process Drains and Wastewater Separations	68.1 kg/160 m^3	(150 lb/42,000 gal) capacity	1400	3000
Blowdown	45 kg/160 m^3	(100 lb/42,000 gal) capacity	900	2000
Relief Valves on Operating Vessels	1.3 kg	(2.9 lb)/day/valve	522	1150
Miscellaneous Losses	4.5 kg/day/160m^3	(10 lb/day/42,000 gal) capacity	90	200
Storage Vessels			1100	2400
		Total	4730	10430

[a] These data apply to plants practicing extensive hydrocarbon control.

Source: Mencher, S.K., "Change Your Process to Alleviate Your Pollution Problem", Petro/Chemical Engineer (21 May 1976), 21.

Table 12 presents wastewater compositions for olefin production with and without oil separation.

Table 12. WASTEWATER COMPOSITION FROM OLEFIN PLANTS

	With Oil Separator	Without Oil Separator
Alkalinity (g/m^3)	1490	-
COD (g/m^3)	500 - 1500	500 - 2000
pH	9.8 - 10.0	4.0 - 8.5
Oil (g/m^3)	-	10 - 300
Phenol (g/m^3)	10 - 50	10 - 50
PO_4 (g/m^3)	10	-
SO_4 (g/m^3)	180	-
Sulfide (g/m^3)	-	0 - 1
TOC (g/m^3)	150 - 700	-
Nitrogen (g/m^3)	60	-
Total Dissolved Solids (g/m^3)	-	5 - 100
Total Solids (g/m)	2140	-

Source: Gloyna, E. F. and D. L. Ford. "The Characteristics and Pollutional Problems Associated with Petrochemical Wastes." Prepared for FWPCA Contract 14-12-461, Ada, Oklahoma: Robert S. Kerr Water Research Center, February 1970.

In addition to the data presented here, quantitative emissions data are included in the process descriptions when available. Where quantitative data are not readily available, a qualitative description of important waste streams is presented.

The types of equipment encountered in this operation are indicated in Table 13. Knowledge of the industry's equipment is often useful in understanding the operations and the magnitude of their emissions. The equipment requirements will vary from plant to plant, but the types of equipment required are basically the same.

Table 13. TYPICAL EQUIPMENT REQUIREMENTS FOR A 500 Gg/YR NAPHTHA CRACKER

	Quantity
Cracking furnaces[a]	16 - 18
Other furnaces	2 - 3
Reactors and dryers	11
Drums	105
Fractionating towers	12
Tanks	6
Pumps and motors	110
Compressors (multistage) and drivers	3
Heat exchangers	200
Miscellaneous (filters, etc.)	100
Piping	4 Gg

Source: Woodhouse, Gordon, et al. "The Economics and Technology of Large Ethylene Projects." Chemical Engineering, 81 (June 1974), 73-85.

[a] Continual improvements are made in equipment design and fabrication methods. These improvements generally result in the use of a smaller number of larger equipment items. Generally, the number of components is related to the age of the plant.

Thermal Cracking

1. Function - A hydrocarbon feed stream (usually natural gas liquids, naphtha, or gas-oil) from a refinery or natural gas processing plant is mixed with steam and heated in a tubular furnace to form a mixed stream of gaseous pyrolysis products. Different feedstocks are cracked in separate furnaces when possible, so that temperatures and steam-to-hydrocarbon ratios can be adjusted for maximum ethylene production.

The tubular furnace used in the majority of thermal cracking operations contains both convection and radiant heating sections. The convection section utilizes flue gas heat to preheat the feed stream while the radiant heating section provides the remainder of the required heat energy. A common arrangement for the radiant section of the furnace is a single row of vertically hung tubes between two fired sidewalls. Horizontal tubes are also common. High temperature alloys of Ni-Cr steel are often used in the radiant section of the furnace because of the excessive temperatures.

The residence time for the gases in the furnance is very short. Older furnances still in use have residence times of thirty (30) seconds; modern furnance residence times may be less than a second. The shorter reaction times favor the primary reactions of producing olefins and diolefins; whereas, longer reaction times promote secondary reactions such as polymerization and aromatics formation. Aromatics formation is especially avoided because the molecules may condense to form polynuclear aromatics and dehydrogenate to form coke which deposits in the tubes.

The pryolysis gases are quickly cooled by passing them through a transfer line heat exchanger (usually of a fixed-tube sheet design, either vertical or horizontal) and then through one or more quenching systems. The transfer line heat exchanger recovers heat as high-pressure steam. If the feedstock is a light stream such as natural gas liquids, the gases may be pumped directly to water quenching (Process No. 3). Heavier feedstock pyrolysis products are sent to oil quenching (Process No. 2).

2. Input Materials - Steam-to-hydrocarbon ratios are commonly adjusted for maximum ethylene recovery. Table 14 gives these ratios for different feedstocks. The steam rate is set to minimize carbon formation in the tubes.

Table 14. STEAM-TO-HYDROCARBON MASS RATIOS

Feed	Steam: Hydrocarbon
C_2/ C_3	0.2 - 0.4:1
Naphthas	0.3 - 0.6:1
Kerosenes & gas-oils	0.5 - 1.0:1

Table 15 presents data concerning feedstock requirements and production in an ethylene plant based on 454 Gg/yr (1 billion lb/yr) ethylene production.

Table 15. FEEDSTOCK AND PRODUCTION DATA

Feedstock	Feedstock Requirement		Product Yields							
			Ethylene		C_3's		C_4's		Gasoline and Fuel Oil	
	Gg/yr	10^6 lb/yr	Gg/yr	10^6 lb/yr	Gg/yr	10^6 lb/yr	Gg/yr	10^6 lb/yr	Gg/yr	10^6 lb/yr
Ethane	568	1250	454	1000	14	31	11	25	9	19
Propane	1030	2270	454	1000	160	353	28	61	88	193
n-Butane	1240	2740	454	1000	227	499	98	216	163	360
Kuwait naphtha	1320	2900	454	1000	178	392	93	205	372	819
Kuwait gas-oil	1570	3460	454	1000	166	365	99	218	622	1371

3. Operating Parameters - Furnace temperatures inside the tubes depend somewhat on feedstock and are usually 800-900°C (1500 to 1600°F).

Typical residence times for modern furnaces are less than one second.

Furnace pressures are usually near atmospheric.

An ethylene plant designed by C. F. Braun & Company generates steam at pressures up to 12 MPa (1800 psi) in the transfer line exchangers. Plants have been designed to produce steam from 1-13 MPa (200-2,000 psi).

Table 16 indicates the heat recoveries possible in the transfer line exchangers.

Table 16. HEAT ENERGY RECOVERED IN TRANSFER LINE HEAT EXCHANGERS

Feedstock	MJ Recovered	Btu Recovered
Ethane	2.2	2100
Propane	3.5	3300
Naphtha	3.6 - 4.2	3400 - 4000

4. Utilities - See Page 32.

Seventy-five percent of the cost of utilities in an ethylene plant is due to fuel consumed by the cracking furnaces.

5. Waste Streams - Combustion gases from the gas-fired furnaces may be fairly high in NO_x content because of high flame temperatures and non-stoichiometric combustion control. NO_x emissions are estimated at 54 kg (120 pounds) per hour. Most furnaces burn sulfur-free plant-produced fuel or sweet natural gas, so that sulfur emissions are very low.

Decoking the furnaces is reported to cause intermittent hydrocarbon and coke particulate emissions to the atmosphere. Coke burning is usually done once a month for several hours. An average of 0.00001 kg of coke particulates is emitted per kg of ethylene produced. Some ethylene plants report scrubbing the decoking gases with water, creating an intermittent wastewater stream. One plant reports a wastewater flow of 5.7 m^3/min (1500 gal/min) from this source.

In response to a questionnaire, one ethylene plant was reported to produce a solid waste stream of 2Mg (5000 lb)/yr of coke which was disposed of in a sanitary landfill.

Emissions from steam generation operations are discussed in the Industry Description. Combustion modifications involving control of fuel-air ratios may be employed to reduce NO_x emissions from furnaces.

6. EPA Source Classification Code - None exists

7. References -

(1) Baba, Theodore B. and James R. Kennedy, "Ethylene and its Coproducts: The New Economics." Chemical Engineering (5 January 1976), 116-128.

(2) Brownstein, Arthur, M., Ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(3) Clancy, Gerald M. Radian Corporation, personal communication (6 February 1976).

(4) Hahn, Albert V. The Petrochemical Industry, Market and Economics. N.Y.: McGraw-Hill Book Company, 1970.

(5) Kent, James A., ed. Riegel's Handbook of Industrial Chemistry. 7th ed. N.Y.: Van Nostrand Reinhold Company, 1974.

(6) Pervier, J.W., et al. Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Vol. II. PB-244 958. ETA No. 450/3-37/005-b. Marcus Hook, Pennsylvania: Air Products and Chemicals, Inc., 1974.

(7) "Petrochemical Handbook." Hydrocarbon Processing, 54 (November 1975), 141-143.

(8) Sittig, Marshall. Pollution Control in the Organic Chemical Industry. Park Ridge, N.J.: Noyes Data Corporation, 1974.

(9) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. 2nd ed. N.Y.: Interscience Publishers. 1965.

(10) Woodhouse, Gordon, et al. "The Economics and Technology of Large Ethylene Projects." Chemical Engineering, 81 (June 1974), 73-85.

(11) Zdonik, S. B., E. J. Bassler and L. P. Hallee. "How Feedstocks Affect Ethylene." Hydrocarbon Processing, 53 (February 1974), 73-81.

(12) Zdonik, S. B., et al. Manufacturing Ehtylene. Tulsa, Oklahoma: Petroleum Publishing Company, 1970.

Oil Quenching

1. Function - Quenching is employed to provide the rapid cooling necessary to retard the secondary reactions which decrease olefin yield and foul the equipment. Quenching devices for naphtha cracking are often proprietary and their mode of performance may be undisclosed. Pyrolysis gases from heavier feedstocks are sometimes cooled by direct contact with quench oil. The gases usually enter the bottom of a vertical quench tower where they are contacted with a countercurrent flow of oil as they flow to the top of the tower. In addition to cooling the gases the quench oil removes entrained hydrocarbon liquids from the pyrolysis products.

The pyrolysis gases then go to a fractionator for removal of fuel oil. The gases from the fractionator go overhead to the water quench tower, while the bottoms are stripped of light oils which are recirculated to the quench tower. The fuel oil is recovered as a by-product and may be used within the plant for steam generation.

2. Input Materials - Pyrolysis gases from the transfer line heat exchangers and quench oil form the input streams to this process.

3. Operating Parameters - For naphtha feedstocks the design outlet temperature of the oil quench tower is 360-520°C, depending on the condition of the tubes (clean or fouled). For gas oil the outlet temperature is 500-650°C. Mass velocities for pressures near 0.2 MPa (2 atm) in the quench tower are 50-70 kg/sec/m^2. The fractionator operates at a pressure near atmospheric.

4. Utilities - See page 32.

5. Waste Streams - Fugitive hydrocarbon emissions may occur at fittings, valves, pumps, etc.

6. EPA Source Classification Code - None exists

7. References -

(1) Baba, Theodore B. and James R. Kennedy. Ethylene and its Co-products: The New Economics." Chemical Engineering (5 January 1976), 116-128.

(2) Clancy, Gerald M. Radian Corporation, personal communication (6 February 1976).

(3) Mol, Alfred and Jan J. Westenbrink. "Steam Cracker Quench Coolers: Their Design and Location." Hydrocarbon Processing, 53 (February 1974), 83.

(4) "Petrochemical Handbook." Hydrocarbon Processing, 54 (November 1975), 141-143.

(5) Radian Corporation. Program to Investigate Various Factors in Refinery Siting. Final Report for Council on Environmental Quality. Contract No. EQC 319. Radian Contract No. 100-029. Austin, Texas: 1974.

(6) Sittig, Marshall. Pollution Control in the Organic Chemical Industry. Park Ridge, N.J.: Noyes Data Corporation, 1974.

(7) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. 2nd ed. N.Y.: Interscience Publishers, 1965.

Water Quenching

1. Function - The pyrolysis gases from light hydrocarbon feedstocks are quenched with water after the heat recovery in the transfer line heat exchangers. Heavy hydrocarbon feedstocks are usually cracked, oil quenched, and then water quenched. Most operations involve a water quenching process at some point. Water quenching cools the gases very rapidly by direct contact with water in a vertical quench tower. Condensable hydrocarbons are also removed in this step. The flow is countercurrent with the gases entering the bottom of the quench tower and cooling water entering the top. The tower may have baffled and tray sections to provide a means of separation of heavier components from the light gases.

The cool, washed gas goes overhead to the compressors, while the condensate goes to a settling drum to effect the separation of quench water from condensed distillate oils. The light oils are sent to further processing; tars are taken out at the bottom for disposal; the hydrocarbon-saturated water is recycled to the quench tower, with the exception of a portion of fouled condensate which is discharged. In many ethylene plants this fouled condensate is stripped to provide a source of water for the dilution steam required in the furnace. This operation reduces the volume of oily water which must go to disposal, but not the total amount of hydrocarbons in the waste stream.

2. Input Materials - Light hydrocarbon feedstock pyrolysis gases from the tubular furnace or heavier hydrocarbon feedstock pyrolysis gases from the fractionation column in the oil quenching process, and cooling water are input materials to this process.

3. Operating Parameters - The following data are for an ethylene plant cracking a C_2/C_3 feedstock to produce 200 Gg/yr (500 x 10^6 lb/yr) with a direct water quench.

Temperature - Inlet gases from the heat exchanger are about 300°C. The baffled section of the vertical tower cools the gases to about 90°C; the gas temperature in the tray section is about 40°C. Variability in water supply will affect temperatures in the quench tower. The settling drum temperature is about 80°C.

Pressure - The pressure at the bottom of the tower is about 159 kPa (8 psig). The settling drum pressure is atmospheric.

Flow rates - The effluent from the heat exchangers enters the quench tower at a rate of 85 Mg/hr (187,000 lb/hr). The cooled gas leaves the tower at a rate of 70 Mg/hr (153,500 lb/hr). Cooling water enters the tower at a rate of 730 Mg/hr (1,600,000 lb/hr). The flow of condensate and water to the settling drum is 750 Mg/hr (1,650,000 lb/hr).

4. Utilities - Make up water for the plant described above is required at the rate of 5.61 Mg/hr (12,350 lb/hr). See page 32.

5. Waste Streams - For the plant described above, 19 Mg/hr (43,000 lb/hr) of fouled condensate is generated. If a stripping operation is included, the resulting waste is 3 Mg (6000 lb)/hr as blowdown. One source reports that the flow rate for untreated fouled condensate may be as high as several thousand liters per minute (hundreds of gallons per minute). Most ethylene plants degas the quenching wastewater stream. The recovered gases are recycled, vented, or flared. When degassing is practiced, continuous atmospheric emissions may result. The amount of tar produced in an ehtylene plant is dependent on the feedstock in use. A naphtha cracking operation reports 0.5 Gg tar produced/Gg of ethylene produced. A non-naphtha cracker reports 0.001 Gg/Gg of ethylene. Some ethylene plants dispose of the tars by landfilling.

6. EPA Source Classification Code - None exists

7. References -

(1) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(2) Pervier, J. W., et al. Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Vol. II. PB-244 958. EPA No. 450/3-37/005-b. Marcus Hook, Pennsylvania: Air Products and Chemicals, Inc., 1974.

(3) Sittig, Marshall. Pollution Control in the Organic Chemical Industry. Park Ridge, N.J.: Noyes Data Corporation, 1974.

(4) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. 2nd ed. N.Y.: Interscience Publsihers, 1965.

Compression

1. Function - The cooled, washed pyrolysis gases are compressed in several stages using single-train certrifugal compressors. It is in this section that refinery gases enter the plant, usually after the first stage of compression. Refinery gas, composed of light ends from crude refining, may contain significant amounts of ethane, ethylene, propane, propylene, and four carbon compounds. The olefins can be recovered and the paraffins can be recycled to the furnaces. This source of olefins is economically competitive with cracking feedstocks if the refinery is located very near the olefins plant.

A common arrangement for the compression train is five stages of compression with an acid gas removal step between the third and fourth stages. After the fifth stage, the gases are desiccated. Condensate from the compression steps is sent to further processing in the fractionation train. Polymer formation and fouling may occur, especially in the first two stages. Some ethylene plants find it necessary to remove acetylenic compounds between the second and third stages. It may be necessary to flush the compressors with a gas-oil to dissolve the polymeric materials formed. The frequency of intermittent compressor cleaning varies with the feedstock. In one plant processing a light hydrocarbon,compressor cleaning is done at 12 to 18 month intervals.

2. Input Materials - Cooled, washed gases from the water quenching process in the ethylene plant are fed to this process. Refinery gas also enters the plant here. The composition of refinery gas varies significantly with refinery feedstocks and operation. A refinery gas composition which would be useful for a feedstock to the ethylene plant is shown in Table 17.

Table 17. COMPOSITION OF A REFINERY GAS[a]

Component	Mole
H_2	12.80
N_2	8.00
CO	2.30
CO_2	2.20
H_2S	1.20
CH_4	33.60
C_2H_4	16.11
C_2H_6	20.20
C_3H_6	2.94
C_3H_8	0.65

[a] This refinery gas has had C_3 and heavier compounds removed.

3. Operating Parameters - Two processes cited in the literature (USC and Lummus) compress the gases to about 3.5-3.9 MPa (500-550 psig).

Compression requirements are approximately 800 W/kg (0.5 brake horsepower/lb) ethylene produced.

4. Utilities - See Page 32

5. Waste Streams - Fugitive emissions may result from compression especially at the compressor seals. One source reports for a plant cracking gas oil and producing 179 Gg/yr (395 x 10^6 lb/yr) of ethylene, an estimated loss of 47 Mg/yr (103,500 lb/yr) or 0.000262 kg emitted per kg of ethylene produced. A water condensate stream from compressor intercoolers may be produced. This aqueous stream contains dissolved hydrocarbons.

6. EPA Source Classification Code - None exists.

7. References -

(1) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(2) Hahn, Albert V. The Petrochemical Industry, Market and Economics. N.Y.: McGraw-Hill Book Company, 1970.

(3) Pervier, J. W., et al. Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Vol. II. PB-244 958. EPA No. 450/3-37/005-b. Marcus Hook, Pennsylvania: Air Products and Chemicals, Inc., 1974.

(4) "Petrochemical Handbook." Hydrocarbon Processing, 50 (November 1971), 152-154.

(5) "Petrochemical Handbook." Hydrocarbon Processing, 54 (November 1975), 141-143.

(6) Sittig, Marshall. Pollution Control in the Organic Chemical Industry. Park Ridge, N.J.: Noyes Data Corporation, 1974.

(7) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. 2nd ed. N.Y.: Interscience Publishers, 1965.

(8) Zondik, S. B., E. J. Bassler and L. P. Hallee. "How Feedstocks Affect Ethylene." Hydrocarbon Processing, 53 (February 1974), 73-81.

Acid Gas Removal

1. Function - Acid gas removal is employed in plants which process sulfur containing feedstocks. Acid gases are removed from the gas stream to a concentration of less than 10 ppm by a combination of amine absorption and caustic scrubbing. The regenerative ethanolamine sorbents have a temperature dependent affinity for hydrogen sulfide. The hydrogen sulfude gas is absorbed and is then released from the sorbent by increasing the temperature.

The compressed gases pass through an absorber tower and are contacted countercurrently with the amine solution. Packed or tray towers are employed. The washed gases go overhead to the caustic scrubber, while the amine solution is pumped to a stripper where the H_2S is removed by heating the rich solution. The amine is preheated by heat exchange with regenerated amine sorbent and is then processed in the stripper column provided with a steam reboiler. The acid gases removed may be flared or vented; very few ethylene plants recover sulfur from the acid gas stream.

The amine-washed pyrolysis gases are scrubbed with a caustic solution by direct countercurrent contact to remove acid gases not absorbed by the amine treatment. This operation may be followed with a water washing step. The scrubbing solution is usually neutralized before it is disposed of; the caustic-washed gases are sent through another compression stage before they are desiccated.

2. Input Materials - Compressed pyrolysis gases, steam, caustic solution and amine sorbent are input materials to this process. Makeup rates for the amine are very low, as it is regenerable.

3. Operating Parameters - The absorber temperature is about 70 to 80°C (160°F to 180°F). The stripper is operated at temperatures about 90°C (200°F).

4. Utilities - See page 32.

5. Waste Streams - The hydrogen sulfide gas from the regenerated amine solution and from the neutralized caustic solution represents one of the biggest pollution potentials for ethylene plants. Unless the plant is associated with a refinery, the gases are usually flared; very few independent operations send them to a sulfur recovery plant. Emissions of sulfur compounds have been reported as high as 0.0012 Mg SO_2/Mg of ethylene produced.

Liquid waste streams result from the caustic scrubbing and water washing operations. The alkaline stream is usually neutralized and ponded. Flow rates of 0.060-0.075 m^3/min (16-20 gal/min) have been reported for caustic streams from ethylene plants. The waste caustic stream production rate has also been reported as 0.063 m^3/Mg (15 gal/ton) of ethylene produced. A typical composition is presented in Table 18.

Table 18. WASTE CAUSTIC STREAM COMPOSITION

NaOH	2.5%
Na_2S	1.0%
Phenols	6.6 ppm
COD	1000 - 2000 g/m^3

Most ethylene plants degas waste caustic and water from the scrubber. This gas may be recycled, vented, or flared and may become a continuous atmospheric emission. Hydrocarbon emissions from the acid gas removal process have been reported as 0.00001 kg/kg ethylene produced.

6. EPA Source Classification Code - None exists.

7. References -

(1) Bland, William F. and Robert L. Davidson, eds. Petroleum Processing Handbook. N.Y.: McGraw-Hill Book Company, 1967.

(2) Pervier, J. W., et al. Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Vol. II. PB-244 958. EPA No. 450/3-37/005-b. Marcus Hook, Pennsylvania: Air Products and Chemicals, Inc., 1974.

(3) "Petrochemical Handbook." Hydrocarbon Processing, 54 (November 1975), 141-143.

(4) Radian Corporation. Program to Investigate Various Factors in Refinery Siting. Final Report for Council on Environmental Quality. Contract No. EQC 319. Radian Contract No. 100-029. Austin, Texas: 1974.

(5) Standom, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. 2nd ed. N.Y.: Interscience Publishers, 1965.

Water Removal

1. Function - The gas from the acid gas removal section of the plant is compressed in the final stage and is then sent to the driers. Dehydration is accomplished by adsorption on alumina or molecular sieves. Typically, two drying towers are onstream in series while a third is being regenerated by heating. Gases (frequently off-gas from the demethanizer or other process gases) are heated and passed through the regenerating bed. The regenerating gases may be directly used as plant fuel. The gases may be cooled to condense the water which becomes a liquid waste stream.

2. Input Materials - Treated pyrolysis gases from the acid gas removal process and a source of regenerating gas are required for this process.

3. Operating Parameters - Not given in information available for this study.

4. Utilities - See page 32.

5. Waste Streams - The water from the driers forms a liquid waste stream which is smaller in volume than that from the inter-stage cooling in the compression process. No information was available concerning treatment or disposal of this wastewater. Spent desiccant forms a solid waste stream which is reported by one plant ot be landfilled at the rate of 30 Mg/yr (66,000 lb/yr).

6. EPA Source Classification Code - None exists.

7. References -

(1) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(2) Pervier, J. W., et al. Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Vol. II. PB-244 958. EPA No. 450/3-37/005-b. Marcus Hook, Pennsylvania: Air Products and Chemicals, Inc., 1974.

(3) Processes Research, Inc. Screening Report, Crude Oil and Natural Gas Production Processes. EPA-R2-73-285, PB-222 718, Contract No. 68-02-0242. Cincinnati, Ohio: 1972.

(4) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. 2nd ed. N.Y.: Interscience Publishers, 1965.

Demethanation

1. Function - In this process the dried gases are refrigerated, compressed and heated in the first of a series of fractionation towers. There are many possible configurations of the tower/refrigeration system. The demethanation step is a determining factor in process efficiency due to ethylene losses in the tower overhead. This step also affects product purity due to the methane content of the tower bottoms.

The chilling train is composed of several refrigeration stages. Refrigeration is usually provided by a propylene-ethylene cascade system. The noncondensables form a hydrogen-rich off-gas which may be used for processing. Alternatively, the entire feed from the water removal process may enter the demethanizer without separation of condensible liquids.

The condensed liquids or gas feed stream are pressured to the first fractionation tower, the demethanizer. This process separates the C_2 and heavier molecules from a methane-rich overhead stream which may be used as fuel after the refrigeration has been recovered by heat exchange or expansion. The demethanizer tower is equipped with a condensing propylene reboiler, and reflux is condensed with ethylene refrigeration. The bottom stream from this tower is fractionated further in the deethanizer.

2. Input Materials - Dehydrated pyrolysis and refinery gases from the driers are input streams to the demethanizer unit. Table 19 presents compositions of typical demethanizer feeds.

Table 19. TYPICAL DEMETHANIZER FEEDS

	Mole Percent	
Component	Feed 1	Feed 2
H_2	26.3	18.9
N_2, CO	-	7.0
CH_4	9.0	26.7
C_2H_4	29.3	19.6
C_2H_6	33.6	16.6
C_3H_6	0.5	5.6
C_3H_8	0.5	4.8
C_4's	0.4	0.7
C_5+	0.4	0.1

3. Operating Parameters - Information found in the literature indicates that demethanizer columns of 20-30 plates may be operated at pressures of 3.0-3.5 MPa (425-500 psig) at a temperature of -70 to -100°C (-100 to -150°F) with a reboiler temperature of 2 to 18°C (35-65°F). Other sources of information indicate a trend toward lower pressures of 280-340 kPa (25 to 35 psig) and temperatures as low as -130°C (-205°).

4. Utilities - See page 32.

The refrigeration system for a naphtha cracker producing 450,000 Mg/yr or ethylene requires 48 MW (65000 brake horsepower).

5. Waste Streams - Fugitive emissions of hydrocarbons may result from seals, valves, and leaks. Intermittent emissions result from relief vents on fractionation towers. The entire fractionation train emits an estimated 0.00050 kg of hydrocarbons per kg of ethylene produced (Processes 7-11).

Refrigeration system waste streams are discussed in the Industry Description.

6. EPA Source Classification Code - None exists.

7. References -

(1) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(2) Hahn, Albert V. The Petrochemical Industry, Market and Economics. N.Y.: McGraw-Hill Book Company, 1970.

(3) Nelson, W. L. Petroleum Refinery Engineering. 4th ed. N.Y.: McGraw-Hill, 1958.

(4) Pervier, J. W., et al. Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Vol. II. PB-244 958. EPA No. 450/3-37/005-b. Marcus Hook, Pennsylvania: Air Products and Chemicals, Inc., 1974.

(5) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. 2nd ed. N.Y.: Interscience Publishers, 1965.

(6) Woodhouse, Gordon, et al. "The Economics and Technology of Large Ethylene Projects." Chemical Engineering, 81 (June 1974), 73-85.

(7) Zdonik, S. B., et al. Manufacturing Ethylene. Tulsa, Oklahoma: Petroleum Publishing Company, 1970.

C_2 Separation

1. Function - This process separates ethane and ethylene from the demethanizer bottoms in three processing steps: deethanizing, acetylene conversion, and C_2 splitting.

The deethanizer produces C_2 compounds as an overhead stream and C_3 and heavier compounds as a bottom stream which is sent to the depropanizer for C_3 separation. This specific fractionation tower is usually equipped with a low-pressure steam reboiler and a refrigerated propylene condenser.

The C_2 fraction taken overhead is treated by selective catalytic hydrogenation in a packed-bed reactor for conversion of acetylene to ethylene. The acetylene concentration must be reduced to a maximum of 10 ppm. The hydrogen necessary for the conversion is often obtained from the demethanizer off-gases. A typical arrangement is two catalytic reactors in parallel, so that one is onstream while the other is being regenerated by heating. Regeneration is an intermittent operation. An alternate arrangement for acetylene removal involves a single bed of a long-life catalyst which does not require regeneration.

The effluent gases from the acetylene converter flow to another fractionation tower in which ethane and ethylene are separated. The C_2 splitter is equipped with a propylene reboiler and a propylene condenser to effect this separation. High purity ethylene (99.9+%) is taken overhead as a product, while ethane is recycled to the cracking furnace. Typical ethylene product specifications are listed in Table 20.

Table 20. TYPICAL ETHYLENE PRODUCT SPECIFICATIONS

Component	Concentration
Ethylene	99.90 - 99.95 mol%
Methane	0.01 - 0.1 mol%
Ethane	0.05 - 0.01 mol%
C_3 and heavier compounds	less than 10 ppm by weight
Acetylene	5-10 ppm by weight
Total sulfur	1-10 ppm by weight
H_2S	1 ppm by weight
H_2	1 ppm by weight
CO	1-5 ppm by weight
CO_2	5-10 ppm by weight
O_2	2-5 ppm by weight
H_2O	5-10 ppm by weight

2. Input Materials - Demethanizer bottoms and hydrogen are input streams to this process.

3. Operating Parameters - Operating conditions will vary from plant to plant. The following data from the open literature are representative.

The deethanizer tower, characterized as a 30- to 40-tray tower by one source and a 100-tray tower by another, operates at -12 to -1.1°C (10-30°F) and 2.2-3.1 MPa (325-450 psia). The reboiler temperature is 68-88°C (155-190°F).

Selective catalytic dehydrogenation is commonly accomplished at 0.5 to 2.5 MPa (50-350 psig) using a noble metal catalyst.

Representative conditions for the C_2 splitter containing 50-65 trays are 1.9-2.4 MPa (275-350 psia), -18 to -29°C (0 to -20°F) tower temperature, and -10 to 4°C (10-40°F) reboiler temperature.

4. Utilities - See page 32.

5. Waste Streams - Fugitive atmospheric emissions of hydrocarbons may occur at seals, valves, vents, and leaks in equipment. Intermittent hydrocarbon emissions are reported at relief vents on fractionation towers. The entire fractionation train (Processes 7-11) emits an estimated 0.00050 kg of hydrocarbons per kg of ethylene produced.

Acetylene converter regeneration has also been reported as a source of intermittent atmospheric emissions containing CO_2 and coke fines.

The regeneration waste gases are sometimes scrubbed with water. The flow rate may be as high as 5.7 m^3/min (1500 gal/min). The operation frequency is about twice yearly for a few days duration. This scrubbing water forms an intermittent liquid waste stream.

Waste streams from refrigeration systems are discussed in the Industry Description.

6. EPA Source Classification - None exists

7. References -

(1) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(2) Nelson, W. L. Petroleum Refinery Engineering. 4th ed. N.Y.: McGraw-Hill, 1958.

(3) Pervier, J. W., et al. Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Vol. II. PB-244 958. EPA No. 450/3-37/005-b. Marcus Hook, Pennsylvania: Air Products and Chemicals, Inc., 1974.

(4) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. 2nd ed. N.Y.: Interscience Publishers, 1965.

C_3 Separation

1. Function - This process isolates propane and propylene from the deethanizer bottoms stream. There are three processing steps involved in effecting this separation: depropanizing, catalytic hydrogenation, and C_3 splitting.

The fractionation tower (called the depropanizer) equipped with a steam reboiler and a water condenser, separates C_3 components from C_4 and heavier fractions which are taken as feed to the C_4 separation process.

The overhead C_3 compounds are passed through a selective hydrogenation step in a packed-bed reactor similar to the acetylene converter in the C_2 separation process. This catalytic reactor converts propadiene and methyl acetylene to propylene. As in the case of the acetylene converter, there are usually two reactors in parallel, so that one may be onstream while one is being regnerated by heating. Alternatively, propadiene and methyl acetylene, which have some commercial value, may be removed as an intermediate sidestream in a fractionator. At this point the propylene content of the gas may be 93%, depending upon the plant operation. A propylene gas of this purity is suitable for chemical grade product and may be marketed. If polymer grade is required, the gases are further processed.

After the alkynes have been removed, the C_3 gases flow to the C_3 splitter equipped with a steam reboiler and a water condenser for separation of propane and propylene. This separation is the most difficult one in the fractionation train; the C_3 splitter may require as many as 200 trays. Polymer grade (99+%) propylene is taken overhead as product, and propane forms the bottoms stream which is recycled to the cracking furnace.

2. Input Materials - Deethanizer bottoms and hydrogen are input streams to this process.

3. Operating Parameters - Representative process conditions for the depropanizer were presented in the literature as 1.0-1.5 MPa (150-225 psia) and 24-43°C (75-110°F) with a reboiler temperature of 107-135°C (225-275°F).

The catalytic converter utilizes a noble metal catalyst to perform the required hydrogenation.

The C_3 splitter may contain up to 200 trays and is operated at 1.9 MPa (260 psig).

4. Utilities - See page 32.

5. Waste Streams - Fugitive atmospheric emissions of hydrocarbon gases may result at valves, seals, and vents. The entire distillation train emits an estimated 0.00050 kg of hydrocarbons per kg of ethylene produced. Intermittent emissions may occur at the relief vents on the fractionation towers. Catalyst regeneration is reported to cause intermittent atmospheric emissions of CO_2 and coke fines. If these gases are scrubbed with water a liquid waste stream results.

Emissions from cooling towers and steam generation boilers are discussed in the Industry Description.

6. EPA Source Classification Code - None exists.

7. References -

(1) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(2) Considine, Douglas M., ed. Chemical and Process Technology Encyclopedia. N.Y.: McGraw-Hill Book Company, 1974.

(3) Nelson, W. L. Petroleum Refinery Engineering. 4th ed. N.Y.: McGraw-Hill, 1958.

(4) Pervier, J. W., et al. Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Vol. II. PB-244 958. EPA No. 450/3-37/005-b. Marcus Hook, Pennsylvania: Air Products and Chemicals, Inc., 1974.

(5) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. 2nd ed. N.Y.: Interscience Publishers, 1965.

C_4 Separation

1. Function - In this process a mixed C_4 stream is isolated from the depropanizer bottoms in a fractionation tower equipped with a steam reboiler and a water condenser. The tower bottoms are pumped to heavy fractionation, while the overhead C_4 stream may be sold to a chemical company or is processed further in the butadiene segment.

2. Input Materials - Depropanizer bottoms form the input to this process.

3. Operating Parameters - Not given in information consulted for this study.

4. Utilities - See Page 32

5. Waste Streams - Fugitive emissions may occur at seals, valves, and vents. The entire fractionation chain emits an estimated 0.00050 kg of hydrocarbons per kg of ethylene produced.

Emissions from cooling towers and from steam generation boilers are discussed in the Industry Description.

6. EPA Source Classification Code - None exists

7. References -

(1) Chemical Technology: An Encyclopedic Treatment, Vol. 4. N.Y.: B&N Import Division, Harper and Row Publishers, Inc., 1972.

(2) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 3. 2nd ed. N.Y.: Interscience Publishers, 1965.

(3) Van Winkle, Matthew. Distillation. U.S.A.: McGraw-Hill Book Co., 1967.

Heavy Fractionation

1. Function - The last process in the fractionation chain is the heavy fractionation. Equipped with a steam reboiler and a water condenser, this tower effects the separation of pyrolysis gasoline from pyrolysis fuel oil. The pyrolysis gasoline, taken overhead, is sent to the BTX Production operation of the Petrochemical Industry for further processing. The bottoms contain pyrolysis fuel oil which is recovered and used as fuel.

2. Input Materials - The bottoms stream from the debutanizer forms the input to this process.

3. Operating Parameters - Not given in information consulted for this study.

4. Utilities - See page 32

5. Waste Streams - Spills and leaks at vents, valves, and seals in equipment are potential sources of emissions in this process. The fractionation train is responsible for an estimated 0.00050 kg of hydrocarbon emissions per kg of ethylene produced.

Waste streams from cooling towers and from steam generation processes are discussed in the Industry Description.

6. EPA Source Classification Code - None exists.

7. References -

(1) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(2) Considine, Douglas M., ed. Chemical and Process Technology Encyclopedia. N.Y.: McGraw-Hill Book Company, 1974.

(3) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. 2nd ed. N.Y.: Interscience Publishers, 1965.

BUTADIENE PRODUCTION PROCESSES

Although butadiene is produced in the industrial organic chemical industry, the importance of production in the petrochemical plant is indicated by the amount of the total production that is recovered from thermal cracking in ethylene plants. Capacities for coproduct recovery in 1976 are 40% of the total capacity for butadiene and are expected to reach 60% by 1980 as more and more cracking of heavier feedstocks is practiced. Producers of butadiene include petrochemical companies as well as chemical and rubber companies. With these facts in mind the decision was made to include an operation for butadiene production in this industry.

Some of the process descriptions were written in a very general manner in an attempt to describe a large number of possible variations in processing methods. This is particularly true in the separation and purification process, which is often more variable than consistent from plant to plant.

Much of the information in the open literature describes post-World War II technology, some of which is considered archaic and is not widely used. The differences in that technology and today's technology lie mainly in the solvent systems and in improved catalysts. These considerations eliminated the discussion of acetonitrile and cuprous ammonium acetate extractive distillation and selective absorption from this treatment, as they are outdated.

This operation, then, is the treatment of a unit called a butadiene plant within a petrochemical complex which produces butadiene by recovery from ethylene plant C_4's and by dehydrogenation of butenes and n-butanes. By-products from the processing include fuel gas, butenes, and isobutylene. The processes necessary for isolating and producing these products are 1) Separation and Purification, 2) Butane Dehydrogenation, and 3) Butenes Dehydrogenation. Figure 6 is a flowsheet of this segment which is included as an aid in understanding the sequence of processes involved.

Quantitative data were not always readily available for operating parameters, utilities, and waste streams. An attempt was made to give a qualitative description of emissions, even though quantifying information was not always found.

One source of information presented the liquid waste composition from one butadiene plant of undesignated processing type in Table 21. Because this table is assumed to include waste streams from the entire plant, it is included here.

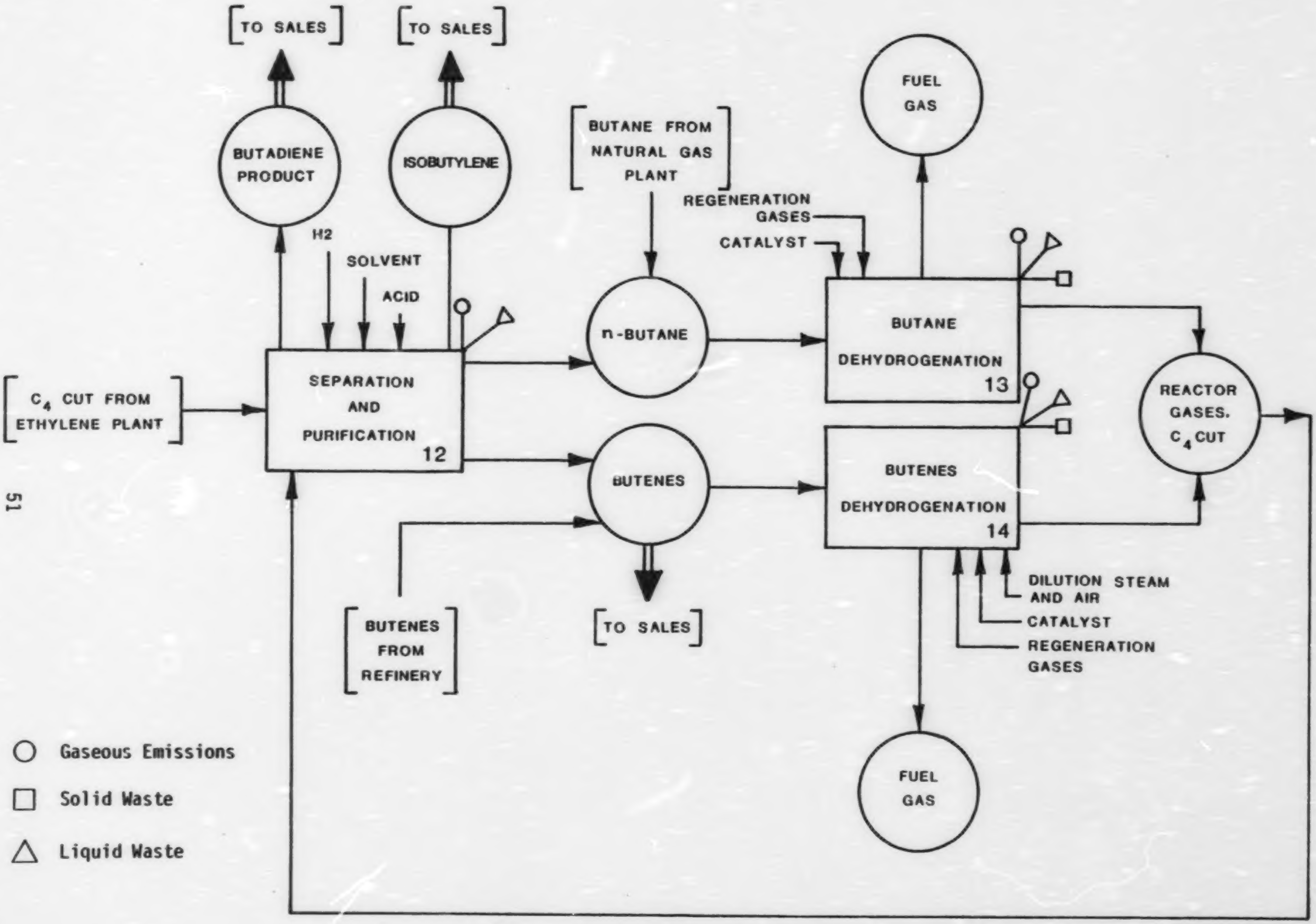

TO SALES
TO SALES
BUTADIENE PRODUCT
ISOBUTYLENE
H2
SOLVENT
ACID
C₄ CUT FROM ETHYLENE PLANT
SEPARATION AND PURIFICATION
12
BUTANE FROM NATURAL GAS PLANT
n-BUTANE
BUTENES
BUTENES FROM REFINERY
TO SALES
REGENERATION GASES
CATALYST
FUEL GAS
BUTANE DEHYDROGENATION
13
BUTENES DEHYDROGENATION
14
DILUTION STEAM AND AIR
CATALYST
REGENERATION GASES
FUEL GAS
REACTOR GASES. C₄ CUT
○ Gaseous Emissions
□ Solid Waste
△ Liquid Waste

Figure 6. BUTADIENE PRODUCTION PROCESSES

Table 21. COMPOSITION OF WASTE FROM A BUTADIENE PLANT[a]

pH	8 - 9
TOC	100 - 200 g/m^3
filtered COD	200 - 375 g/m^3
suspended solids	200 - 500 g/m^3
total solids[b]	3000 - 4000 g/m^3

[a] Flow rate 0.417 m^3/Mg (100 gals/ton of product)

[b] Mostly sulfates and chlorides

Source: Gloyna, E. F. and D. L. Ford. "The Characteristics and Pollutional Problems Associated with Petrochemical Wastes." Prepared for FWPCA Contract 14-12-461, Ada, Oklahoma: Robert S. Kerr Water Research Center, February 1970.

Separation and Purification

1. Function - A mixed C_4 stream is transferred from the olefins plant to be separated into products for further processing in the butadiene plant. Reaction products from the dehydrogenation reactors are also fractionated and purified in this process. There are three main processing steps involved: 1) separation of butane, butenes, and butadiene, 2) isobutylene removal, and 3) acetylenics removal. The butane and butenes produced in this process are sent to dehydrogenation (Processes 13 and 14) and butadiene and isobutylene are recovered for sales.

The boiling point temperatures of four carbon compounds are too close together to allow separation by regular fractional distillation. A series of extractive distillations and selective absorptions is required. A number of solvents have been used to aid fractionation by modifying the volatilities of the C_4 compounds. There are many possible variations in separation processing sequences depending on the solvent selected and the composition of the input streams. The inherent complexity and possible variability is indicated by describing the separation process using furfural as the solvent.

A distillation tower splits the feed into butadiene and 1-butene overhead and n-butane-butenes mixture as bottoms. The overhead streams are sent to an extractive distillation column in which a butadiene solvent mixture forms the tower bottoms. The solvent is stripped, and another distillation column removes the final traces of solvent from the butadiene product. The n-butane-butenes bottoms stream from the feed splitter is fed to another series of extractive and conventional distillation columns. Some solvent systems require a water washing step to free the stream from solvent. The absorbers and strippers which accompany the distillation columns allow solvent recovery and recycle. Recovered butadiene may be further purified in a molecular sieve bed. The isolated butenes may be sold as a chemical product, but most of the butenes and the butane are consumed in butadiene manufacture.

The removal of isobutylenes is necessary as they will not dehydrogenate in the reactors and the concentration will continually build in the plant stream. Separation is accomplished by extraction with 60-65% cold sulfuric acid. The acid is regenerated either by stripping the isobutylenes, which may be sold as a chemical product, or by oligomerization of the hydrocarbon to an acid-insoluble product useful for gasoline blending.

The tendency of acetylenics to coke and form deposits in the catalyst beds makes their removal necessary. The extraction distillation system employing dimethylformamide eliminates the need for this operation, but other solvent systems require selective catalytic hydrogenation to convert the acetylenics to olefins. A vapor-phase process is generally used.

2. Input Materials - The C_4 stream from ethylene plants and the recycle dehydrogenation products are feed streams to this process. Yields of butadiene from thermal cracking vary with the feedstock in use as shown in Table 22. Hydrogen is required as a feed stream to the catalytic hydrogenation of the acetylenic compounds. The content of acetylenic molecules of various streams is illustrated in Table 23. Makeup requirements for acid and extractive solvents are probably low, since recycle methods are practiced. Some of the common solvents in current use are dimethylacetamide, dimethylformamide, acetonitrile, N-methylpyrrolidone, and furfural.

Table 22. BUTADIENE YIELDS FROM THERMAL CRACKING[a]

Feedstock	kg Butadiene per 100 kg of Ethylene Produced
Ethane	2.5
Propane	7.1
n-Butane	8.7
Medium range naphtha	13.6
Reformer raffinate (C_6-C_8)	16.8
Atmospheric gas-oil	17.6
Light vacuum gas-oil	24.7

[a] Data are based on production of 454 Gg/yr (1 x 10^9 lb/yr) of ethylene with high severity cracking and ethane recycle.

Table 23. ACETYLENICS CONTENT OF VARIOUS C_4 STREAMS

Source	Acetylenics Concentration in ppm by Weight
Thermal cracking	2500 - 5000
Dow B Butene dehydrogenation	1000 - 3000
Shell 205 Butene dehydrogenation	500 - 750
Houdry n-Butane dehydrogenation	200 - 500

3. Operating Parameters - The important operating parameters are temperature, pressure, and solvent system. Different combinations of these parameters effect different separations. Specific data concerning operating parameters were not available in the references consulted for this study. A wide range of conditions is expected.

4. Utilities - Quantitative utility requirements are unavailable in the sources consulted for this study. Steam is required for reboilers and strippers; energy is required for pumping various plant streams; and cooling water is required for condensers.

5. Waste Streams - Wastewater is generated in some plants in the solvent recovery operation, notably in furfural solvent systems. Wastewater characteristics of several different butadiene plants are presented in Table 24. The wastewater characteristics from dehydrogenation and from recovery of butadiene from ethylene by-products are essentially the same. The variation in total wastewater flows is due to the use of steam ejectors with barometric condensers to produce reactor vacuum. Plants 1 and 2 use processes which operate at low pressures (see Process 13, Houdry Process).

Table 24. WASTEWATER FROM BUTADIENE PLANTS

Process	Flow		COD(g/m^3)	BOD$_5$(g/m^3)	TOC(g/m^3)
	m^3/Mg	(gal/1000 lb)			
Plant 1 Dehydrogenation, extractive distillation	9.67	(1160)	334	306	-
Plant 2 Dehydrogenation, extractive distillation	12.1	(1451)	20,200	5,960	-
Plant 3 Coproduct of ethylene, extractive	0.734	(88)	1,525	745	755
Plant 4 Coproduct of ethylene, extractive distillation	1.53	(183)	683	102	205

Fugitive and intermittent hydrocarbon emissions in gaseous and liquid form may occur in absorbers, fractionaters, and strippers at valves, vents, pump seals, compressor seals, and leaks in the equipment. Hydrocarbons may be composed of feed or product stream components as well as solvent degradation products.

Emissions from cooling towers and from steam boilers are discussed in the Industry Description.

6. EPA Source Classification Code - None exists.

7. References -

(1) "Butadiene," 620.5022 A. Chemical Economics Handbook. Menlo Park, California: Stanford Research Institute, 1974.

(2) Environmental Protection Agency (Office of Water and Hazardous Materials, Effluent Guidelines Div.). Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category. EPA 440/1-74-009-a. Washington, D.C.: 1974.

(3) Hahn, Albert V. The Petrochemical Industry, Market and Economics. N.Y.: McGraw-Hill Book Company, 1970.

(4) Hedley, W. H., et al. Potential Pollutants from Petrochemical Processes. MRC-DA-406. Dayton, Ohio: Monsanto Research Corp., December 1973.

(5) Kent, James A., ed. Riegel's Handbook of Industrial Chemistry. 7th ed. N.Y.: Van Nostrand Reinhold Company, 1974.

(6) Sittig, Marshall. Pollution Control in the Organic Chemical Industry. Park Ridge, N.J.: Noyes Data Corporation, 1974.

(7) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 3. 2nd ed. N.Y.: Interscience Publishers, 1965.

Butane Dehydrogenation

1. Function - Butane feed separated from the mixed ethylene plant C_4 stream is supplemented with butane from a natural gas plant to be catalytically dehydrogenated in a one- or two-step process.

The Houdry Catadiene process is a one-step dehydrogenation process producing a mixture of butadiene and butenes whose composition can be varied by varying the operating conditions. This type of processing sequence requires banks of three to eight brick-lined reactors filled with a catalyst of aluminum oxide carrying chromium oxide mixed with alumina particles acting as heat carriers. The reactors operate on cycles of reaction, regeneration, and purge. Regeneration is accomplished with steam and heated air, while the purging cycle utilizes fuel gas to treat the catalyst under reducing conditions. The resulting gases contain unreacted butane, butenes, butadiene, and by-product gases.

The Phillips two-stage process dehydrogenates butane to butenes in one stage, utilizing a second stage (Process No. 14) to convert the butenes to butadiene. After thorough drying of the input stream, the isothermal dehydrogenation of butane is accomplished in tubular reactors filled with alumina-chromia catalyst. As in the Houdry process, the operation is cyclic, so that a parallel arrangement is advantageous with one reactor onstream while another is being regenerated with a mixture of air and flue gas. The product gases from the reactor contain butenes and unreacted n-butane along with some by-product gases.

The gases from the reactor are quenched with oil (See Process No. 2) and compressed. The C_4 compounds are separated from light gases (H_2, CO, CO_2, CH_4, C_2's, and C_3's) by fractional distillation using one or more towers. The off-gases are generally used for fuel, as they amount to about 20% of the reactor gases. Another possibility is that hydrogen may be recovered for use in hydrogenating acetylenics before the gas is used as fuel. Propylene is recovered from this stream in at least one installation. The ultimate usage of the gas must be dictated by local operations and economics. The mixed C_4 stream is returned to the separation and purification process (Process No. 12) for isolation of the C_4 products.

2. Input Materials - The Houdry process requires 1.7 to 1.9 kg of 95+% butane feed per kg of butadiene produced. The yield is 57-63%. Steam, hot air, and fuel gas are required for regeneration of the catalyst beds.

The Phillips process requires a desiccant, often bauxite. The preferred feed material is 98% n-butane which is 30% converted with 80% selectivity toward butene and butadiene.

3. Operating Parameters - The Houdry dehydrogenation process requires a temperature of 600°C (1100°F), a pressure of 10-20 kPa (2-3 psia) with a space velocity of 2 (liquid volume/hr/volume of catalyst). Onstream time is 4-10 minutes; the total reaction and regeneration cycle requires about 15 minutes.

Operating conditions for the Phillips process are 560-590°C (1050-1100°F) and 100-200 kPa (1-20 psig) with a space velocity of 700 liquid volume/hr/volume of catalyst. The onstream time is approximately one hour with a one-hour regeneration cycle. Regeneration takes place at 800 kPa (100 psig) with an air-flue gas mixture containing 2-3% oxygen.

Both processes use chromium oxide/aluminum oxide catalysts.

4. Utilities - Utility requirements for a Houdry Catadiene process treating normal butane or isobutane to produce 993 m^3/stream day (6250 bbl/stream day) of 55% butylenes are summarized as follows:

Electricity:	150 kWh/m^3 product (24 kWh/bbl product)
Steam:	340 kg/m^3 (120 lb/bbl)
Fuel:	730 MJ/m^3 (110×10^3 Btu/bbl)
Cooling water:	52.2 m^3/m^3 (2190 gal/bbl)

5. Waste Streams - Catalyst regeneration causes intermittent emissions of CO_2 and coke and catalyst fines. It is assumed that spent catalyst is landfilled. When regeneration gases are scrubbed with water, an intermittent wastewater stream results.

Steam ejectors with barometric condensers may be used to produce a vacuum in the reactor. These systems generate a huge wastewater stream which may be eliminated by the use of vacuum pumps.

Fugitive hydrocarbon emissions may result at vents, valves, seals, and leaks in equipment. Intermittent hydrocarbon emissions may occur at emergency relief vents on fractionation towers.

Waste streams from steam generation are discussed in the Industry Description.

6. EPS Source Classification Code - None exists.

7. References

(1) Bland, William F. and Robert L. Davidson, eds. Petroleum Processing Handbook. N.Y.: McGraw-Hill Book Company, 1967.

(2) "Catadiene." Hydrocarbon Processing, 49 (September 1970), 265.

(3) Environmental Protection Agency (Office of Water and Hazardous Materials, Effluent Guidelines Div.). Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category. EPA 440/1-74-009-a. Washington, D.C.L 1974.

(4) "Petrochemical Handbook." Hydrocarbon Processing, 50 (November 1971), 136-137.

(5) Sittig, Marshall. Pollution Control in the Organic Chemical Industry. Park Ridge, N.J.: Noyes Data Corporation, 1974.

(6) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 3. 2nd ed. N.Y.: Interscience Publishers, 1965.

Butenes Dehydrogenation

1. Function - Butenes may be catalytically dehydrogenated to butadiene in fixed-bed reactors. In plants installed prior to 1970 catalytic dehydrogenation of n-butenes is accomplished via endothermic processes. The purified butene feed is mixed with steam to achieve the high temperature required and to minimize coke formation. Two commonly used catalysts are Shell 205 and Dow B. Regeneration of the Shell 205 catalyst is with superheated steam; regeneration of Dow B is accomplished with a mixture of steam and air. If a Dow B catalyst is used, special purification equipment may be required to remove acetylenics and carbonyl by-products which are toxic and may require special treatment before disposal. Recoverable quantities of acetone and methylethyl ketone are produced.

Recently, exothermic oxidative dehydrogenation processes have been developed including the Petrotex process and the second stage of the Phillips process, which employs a halogen promoted catalyst. The butenes from the separation process are mixed with compressed air and steam and passed over the catalyst bed to effect the conversion to butadiene. A process licensed by BP International utilized multitubular reactors filled with mixed oxide catalyst. The heat developed is used in making steam. The reported onstream time is several thousand hours.

The dehyrogenation reaction gases are quenched with oil (Process 2), compressed, and the light gases are removed from the C_4 compounds which are recycled to the separation and purification process (Process No. 12) for isolation of the C_4 compounds. The light gases are generally used as fuel; hydrogen may be recovered for use in acetylenics removal by hydrogenation.

2. Input Materials - Butenes from the separation process and from refineries along with steam and air are feed streams to this process. Catalyst makeup rates are assumed to be very low.

Shell 205 catalyst requires 8 moles of dilution steam per mole of butene; Dow B requires 18-20 moles dilution steam per mole of butene.

3. Operating Parameters - Table 25 contains operating parameters for dehydrogenation with Dow B and Shell 205 catalysts. Operating conditions for the oxidative dehydrogenation were not readily available in the information consulted for this study.

Table 25. OPERATING PARAMETERS FOR DEHYDROGENATION OF BUTENES

	Shell 205	Dow B
Temperature	620 - 680°C	590 - 680°C
Space velocity	500/hrs	125 - 175/hrs
Operating pressure	atmospheric	170 - 200 kPa (10-15 psig)
Regeneration pressure	450 kPa (50 psig)	
Catalyst type	ferric oxide, chromium oxide, potassium oxide	calcium nickel phosphate stabilized with chromium oxide
Regeneration frequency	1 hr/day	15 min/30 min
% conversion[a]	26 - 28	up to 45
% selectivity[b]	73 - 75	90

[a] (butene disappearing/butene feed/pass) X100

[b] (moles butadiene produced/moles butene disappearing) X100

4. Utilities - The endothermic dehydrogenation process requires about 1.7 MJ/kg (720 Btu/lb) of converted butenes as heat energy.

Utilities for an endothermic process for dehydrogenating butenes are given below based on 45 Mg/yr (100,000 lb/yr) capacity.

Cooling water - 163 m^3/min (43,130 gal/min)
Process and makeup water - 7.1 m^3/min (1,870 gal/min)
Power - 10.9 MW (14,600 hp)
Water refrigeration - 801 W (2,735 tons)
Ammonia refrigeration - 533 W (1,820 tons)
Steam (4.2 mPa, 400°C) - 10.9 Mg/hr (24,000 lb/hr)
Natural gas - 8,660 m^3/hr (306,000 ft^3/hr)

5. Waste Streams - No quantitative data were available for emissions from the dehydrogenation of butenes in the literature consulted for this study.

Catalyst regeneration causes intermittent emissions of CO_2, coke fines, and catalyst fines. If the regeneration gases are scrubbed with water, an intermittent wastewater stream results.

It is assumed that spent catalyst is landfilled.

Toxic oxygenated by-products of some catalyst systems may be vented to the atmosphere or discharged with wastewater unless a treatment method is utilized.

Emissions from steam generation processes are discussed in the Industry Description.

6. EPA Source Classification Code - None exists

7. References -

(1) "Butadiene," 620.5022 A. Chemical Economics Handbook. Menlo Park, California: Stanford Research Institute, 1974.

(2) Environmental Protection Agency (Office of Water and Hazardous Materials, Effluent Guidelines Div.). Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category. EPA 440/1-74-009-a. Washington, D.C.: 1974.

(3) Hahn, Albert V. The Petrochemical Industry, Market and Economics. N.Y.: McGraw-Hill Book Company, 1970.

(4) Hedley, W. H., et al. Potential Pollutants from Petrochemical Processes. MRC-DA-406. Dayton, Ohio: Monsanto Research Corp., December 1973.

(5) "Petrochemical Handbook." Hydrocarbon Processing, 50 (November 1971), 136-137.

(6) Sittig, Marshall. Pollution Control in the Organic Chemical Industry. Park Ridge, N.J.: Noyes Data Corporation, 1974.

(7) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 3. 2nd ed. N.Y.: Interscience Publishers, 1965.

BTX PRODUCTION PROCESSES

This operation of the basic petrochemicals industry is composed of processes which produce benzene, toluene, mixed xylenes, and the separate xylene isomers for use as solvents, chemical intermediates, or gasoline blending stocks. The two feedstocks processed in this industry operation are the C_6-C_9 fraction of catalytic reformate from refineries and the pyrolysis gasoline by-product of olefins production by thermal cracking. Although a few companies produce BTX from purchased coke oven light oil, benzene, toluene, and xylenes are produced from coal tar and coke oven by-products in a separate industry. BTX production processes utilizing coal-derived feedstocks are not included in this industry.

Figure 7 illustrates the nine processes utilized in BTX production from catalytic reformate and pyrolysis gasoline. The first three processes include (1) hydrotreating of pyrolysis gasoline, (2) extraction of aromatics from reformate and pyrolysis gasoline, and (3) fractionation of the aromatic extract to produce pure benzene, toluene, and a mixture of C_8 aromatics.

Further processing of toluene and mixed xylenes includes a number of alternatives. One source indicates that of thirty-three companies producing BTX, twelve also produced one or more separate isomers from mixed C_8 aromatics by employing some combination of Processes 18 through 21. For illustrative purposes all four processes are shown in the combination in Figure 7. In practice various combinations are employed in order to maximize production of a particular isomer. Para-xylene and ortho-xylene have the largest market for chemical intermediate use, but meta-xylene occurs naturally in the highest concentration. Mixed xylenes are widely used as solvents and in gasoline blending. Thus, the processing scheme employed depends on the value of solvent xylenes or gasoline blending components as well as the cost of isomerization and separate isomer recovery for chemical intermediate use. Technology is still in the early years of commercialization for some isomer separation methods. Complexation processes employing nickel thiocyanate/β-picoline, $Ni(4\text{-methylpyridene})_4(SCN)_2$, metal adducts, and carbon tetrachloride are mentioned in the literature, but there is insufficient information for preparation of process descriptions. Processes also exist involving selective sulfonation and hydrolysis and three-phase crystallization. The extent of application of these processes is not evident.

Toluene processing options include gasoline blending, production of benzene by dealkylation (Process 23), production of mixed xylenes by disproportionation (Process 22), and limited markets for chemical intermediate use. Dealkylation capacity exists but may not be current use. It is not clear whether disproportionation capacity is available in the U.S. As in the case of mixed xylenes, further toluene processing depends on the comparative economics for producing and selling the possible products.

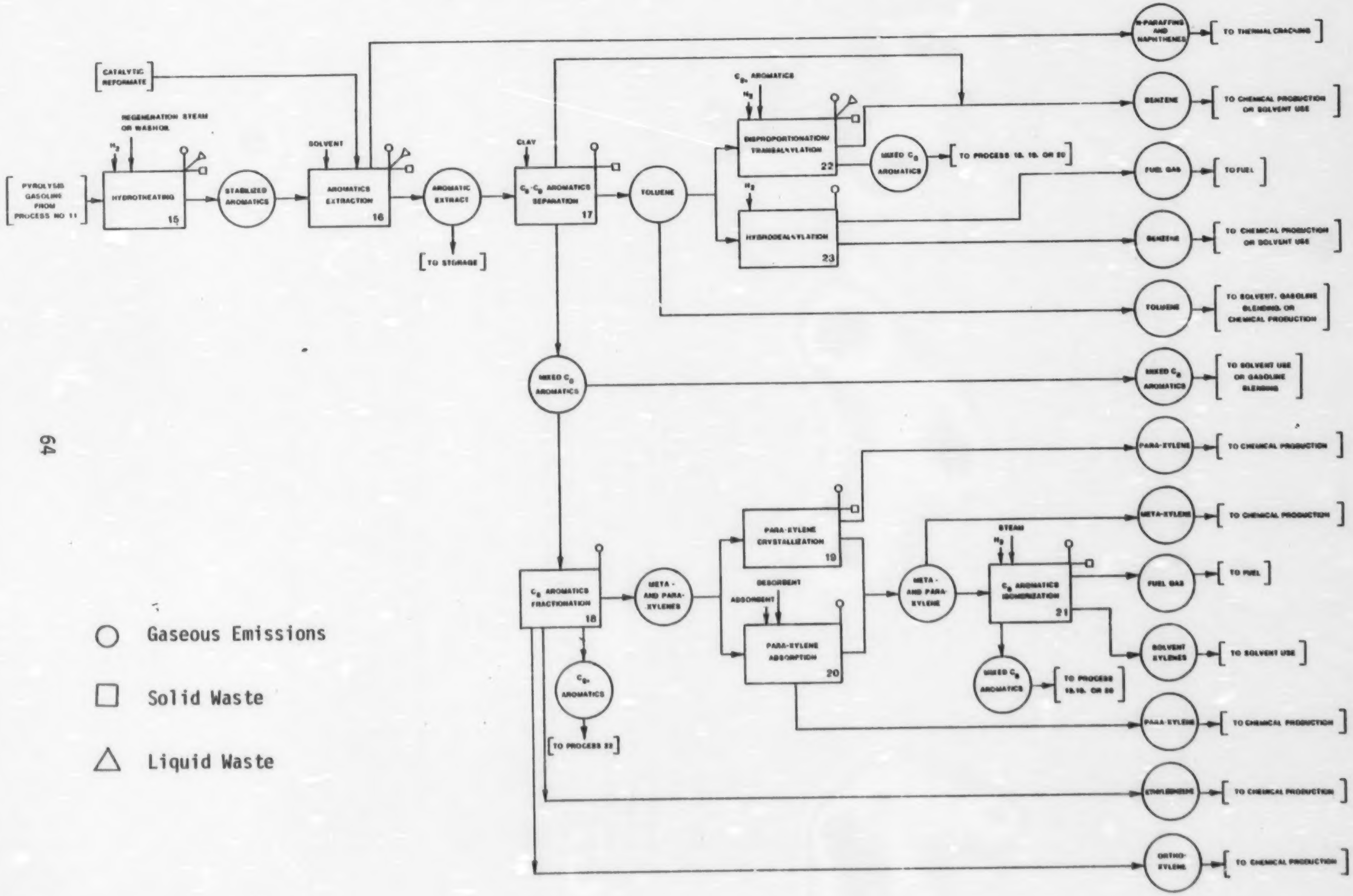

PYROLYSIS GASOLINE FROM PROCESS NO 11
CATALYTIC REFORMATE
H_2
REGENERATION STEAM OR WASHOIL
HYDROTREATING
15
STABILIZED AROMATICS
SOLVENT
AROMATICS EXTRACTION
16
AROMATIC EXTRACT
TO STORAGE
CLAY
C_6-C_8 AROMATICS SEPARATION
17
TOLUENE
C_{9+} AROMATICS
H_2
DISPROPORTIONATION/ TRANSALKYLATION
22
H_2
HYDRODEALKYLATION
23
MIXED C_8 AROMATICS
TO PROCESS 18, 19, OR 20
MIXED C_8 AROMATICS
C_8 AROMATICS FRACTIONATION
18
C_{9+} AROMATICS
TO PROCESS 22
META- AND PARA-XYLENES
PARA-XYLENE CRYSTALLIZATION
19
DESORBENT
ADSORBENT
PARA-XYLENE ABSORPTION
20
META- AND PARA-XYLENE
STEAM
H_2
C_8 AROMATICS ISOMERIZATION
21
MIXED C_8 AROMATICS
TO PROCESS 18,19, OR 20
N-PARAFFINS AND NAPHTHENES
TO THERMAL CRACKING
BENZENE
TO CHEMICAL PRODUCTION OR SOLVENT USE
FUEL GAS
TO FUEL
BENZENE
TO CHEMICAL PRODUCTION OR SOLVENT USE
TOLUENE
TO SOLVENT, GASOLINE BLENDING, OR CHEMICAL PRODUCTION
MIXED C_8 AROMATICS
TO SOLVENT USE OR GASOLINE BLENDING
PARA-XYLENE
TO CHEMICAL PRODUCTION
META-XYLENE
TO CHEMICAL PRODUCTION
FUEL GAS
TO FUEL
SOLVENT XYLENES
TO SOLVENT USE
PARA-XYLENE
TO CHEMICAL PRODUCTION
ETHYLBENZENE
TO CHEMICAL PRODUCTION
ORTHO-XYLENE
TO CHEMICAL PRODUCTION
○ Gaseous Emissions
□ Solid Waste
△ Liquid Waste

Figure 7. BTX PRODUCTION PROCESSES

Hydrotreating

1. Function - This catalytic hydrogenation process treats raw pyrolysis gasoline from thermal cracking to produce a stabilized mixed aromatics stream for input to mixed aromatics extraction. Pyrolysis gasoline contains mono-olefins, diolefins, and sulfur and nitrogen compounds which are removed by hydrotreating in such processes as Unifining (U.O.P.) and HPG (Houdry-Gulf). Two hydrotreating stages are employed. The first involves a low temperature reaction in which gumforming diolefins are saturated. In the conventional second-stage hydrotreater, mono-olefins are saturated, and sulfur and nitrogen compounds are converted to H_2S and NH_3.

Processing steps and equipment include the following:

- Hydrogen and pyrolysis gasoline feedstock are preheated by steam or by exchange with reactor effluent.
- First-stage liquid or gas-phase hydrotreating is accomplished, probably in a fixed-bed catalytic reactor.
- The first-stage effluent is heated. A furnace (fired heater) is employed in one process.
- The second-stage hydrotreater employs conventional refinery hydrotreating technology.
- The second-stage hydrotreater effluent is cooled. One process employs a water-cooled heat exchanger.
- A gas-liquid separator is employed to produce a hydrogen-rich stream for recycle. Caustic scrubbing may be employed for purification of the hydrogen recycle stream.
- The liquid stream from the separator is treated in a stabilizer-stripper which removes dissolved inorganic gases and light hydrocarbons. This may be accomplished by reduced pressure or steam stripping.
- If water is injected to remove ammonium bisulfate salts and coke particles, a coalescer is employed to separate the wastewater.

2. Input Materials - Pyrolysis gasoline, which may contain up to 80% aromatics, and hydrogen are the input materials. The composition of pyrolysis gasoline from thermal cracking depends on the cracking feedstock and the process conditions. Table 26 shows the hydrocarbon analysis for a typical pyrolysis gasoline. Table 27 illustrates feed and product compositions for a published design case. Stoichiometric hydrogen requirements for the design case were 48.9 normal m^3/m^3 (300 scf/bbl) pyrolysis gasoline. An empirical correlation of stoichiometic hydrogen consumption with pyrolysis gasoline properties such as Diene Value, specific gravity and bromine number is available in the literatuere.

Table 26. HYDROCARBONS IN TYPICAL PYROLYSIS GASOLINE CONTAINING 70% AROMATICS

Component	Weight Percent of Total Hydrocarbons
Diolefins	15
Mono-olefins	8
Saturates	7
Benzene	32
Toluene	14
C_8 Aromatics	11
C_9+ Aromatics	13
	100

Source: Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

Table 27. DESIGN CASE COMPOSITION OF FEED AND PRODUCT FROM TWO-STAGE HYDROGENATION OF PYROLYSIS GASOLINE FOR SULFUR AND GUM REMOVAL

Component (wt %)	Feed	Product
Benzene	37.2	37.3
Toluene	21.2	21.1
Ethylbenzene	1.5	6.0
Meta-, para-xylene	4.4	4.5
Ortho-xylene	1.2	1.2
Styrene	4.6	not given
Sulfur (wt ppm)	150	<1
Gum ($kg/100m^3$)	<10	0

Source: Kubo, Haruo, Shinobu Masamune and Ryoji Sako. "Make B.T.X. From Cracker Gasoline." Hydrocarbon Processing, 49 (July 1970), 111.

3. Operating Parameters - The first-stage hydrotreater is operated at 150-200 C° (300-400°F) with nickel sulfide or platinum catalysts. The second-stage hydrotreater temperature range is 300-400°C (600-800°F). A cobalt-molybdenum catalyst is used.

4. Utilities - The design case process described in Table 27 employs steam preheating; a low-temperature, liquid-phase first-stage hydrotreating process; a furnace for heating first-stage hydrotreater effluent; a water-cooled heat exchanger for cooling second-stage hydrotreater effluent; and a compressor for recycle hydrogen. Utility requirements for a plant of this design with a capacity of 182,000 Mg/yr are given in Table 28.

Table 28. UTILITY REQUIREMENTS FOR 182,000 METRIC TON/YR TWO-STAGE PYROLYSIS GASOLINE HYDROTREATER

Utility	Value Per Barrel of Pyrolysis Gasoline
Electric Power	2.96 kWh
500 kPa (60 psig) Saturated Steam	17.9 kg (39.2 lb)
Fuel	42.8 MJ (40.5×10^3 Btu)
Cooling Water ($\Delta T = 10^\circ C = 18^\circ F$)	4.527 m^3 (1196 gal)

Source: Kubo, Haruo, Shinobu Masamune and Ryoji Sako. "Make B.T.X. From Cracker Gasoline." Hydrocarbon Processing, 49 (July 1970), 111.

5. Waste Streams - Intermittent waste streams originate from catalyst cleaning. Relatively frequent catalyst fouling in the first-stage hydrotreater is a problem and accounts for some of the variations in the available processes. Wash oil is used to dissolve polymerized material from the catalyst in the HPG process. Hydrogen stripping and steam-air decoking, which are employed in other processes, produce gaseous emissions containing carbon monoxide. Steam-air decoking may be required at four-month intervals, while a six- to nine-month regeneration cycle has been estimated for other processes. One process claims a two- to three-year catalyst life on the basis of pilot plant operations.

Dissolved NH_3, H_2S, and light hydrocarbons are separated from the hydrotreated liquid in the stabilizer-stripper section. If a low-pressure separator is used, a gaseous waste stream is produced. Neither the concentrations of pollutants nor the disposition of this gas stream were evident from the literature. In refinery hydrodesulfurization (see Chapter 3, Process No. 16), this stream is treated by amine scrubbing for H_2S removal and then used as fuel. Alternatively, steam stripping may be employed to remove H_2S in the stabilizer section. This operation produces a sour water waste stream. In refinery operations (see Chapter 3) this stream is treated in a sour water stripper.

Additional intermittent wastewater streams may be produced. Water may be used for alkaline scrubbing of the hydrogen recycle stream. Blowdown will produce wastewater. The hydrotreated liquid may be washed to remove ammonium salts originating from hydrogenation of nitrogen compounds and coke particles from pyrolysis. Wash water will be separated from the liquid product by a coalescer.

Table 29 shows wastewater characteristics which resulted from measurements on process streams at a pyrolysis gasoline hydrotreating facility. These characteristics were proposed as representative of the industry.

Table 29. CHARACTERISTICS OF WASTEWATER FROM TWO-STAGE HYDROTREATING OF PYROLYSIS GASOLINE

Characteristic	Concentration g/m^3	Volume or Weight per Mg of Product
Wastewater Flow		$0.114 m^3$
Five-day BOD	914	0.10 kg
COD	2755	0.31 kg
TOC	306	0.03 kg

Source: Environmental Protection Agency (Office of Water and Hazardous Materials, Effluent Guidelines Div.). Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemicals Manufacturing Point Source Categoy. EPA 440/1-74-009-a. Washington, D. C.: 1974.

6. EPA Source Classification Code - None exists.

7. References -

(1) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(2) Considine, Douglas M., ed. Chemical and Process Technology Encyclopedia. N.Y.: McGraw-Hill Book Company, 1974.

(3) Environmental Protection Agency (Office of Water and Hazardous Materials, Effluent Guidelines Div.). Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category. EPA 440/1-74-009-a. Washington, D. C.: 1974.

References (Cont'd)

(4) Hahn, Albert V. The Petrochemical Industry, Market and Economics. N.Y.: McGraw-Hill Book Company, 1970.

(5) Kubo, Haruo, Shinobu Masamune and Ryoji Sako. "Make B.T.X. From Cracker Gasoline." Hydrocarbon Processing, 49 (July 1970), 111.

(6) "Refining Handbook." Hydrocarbon Processing, 53 (September 1974), 153

(7) Sittig, Marshall, Pollution Control in the Organic Chemical Industry. Park Ridge, N.J.: Noyes Data Corporation, 1974.

Aromatics Extraction

1. Function - This process extracts aromatics from hydrocarbon mixtures such as catalytic reformate and pyrolysis gasoline. The technology was first employed in refineries to produce nitration grade aromatics from catalytic reformate. The Udex process, employing di-, tri-, or tetra-ethylene glycol-water mixtures, and the Sulfolane process are the methods most commonly used. Approximately equal numbers of Udex and Sulfolane units were in operation in 1972. The products are a mixed aromatics extract, which is stored, and raffinate, containing mainly paraffins, which may be treated by thermal cracking or used as a solvent or jet fuel component.

Udex Process - Udex processing steps include countercurrent extraction in a trayed or rotating disk contactor, separation of solvent from aromatics in the extractor bottoms stream by steam stripping, condensation of stripped aromatic vapors in an extract receiver, and water washing of both the extractor overhead (raffinate) and the extract to recover traces of glycols. Wash water is treated in a water-solvent still and recycled. The separated solvent is regenerated and recycled. Regeneration produces a sludge waste stream.

Sulfolane Process - The Sulfolane process also employs countercurrent extraction. Rich solvent is treated in an extractive stripper. Stripper overhead vapors are condensed, and the hydrocarbon components are separated from the aqueous solvent and recycled to the extractor. Stripper bottoms and aqueous solvent are charged to an extract recovery column. Lean solvent from the recovery column is recycled. Solvent-free extract is condensed from the extract recovery column overhead stream. Using water from the extract accumulator, raffinate is water washed to remove solvent.

2. Input Materials - Input materials are mixed aromatics and solvent. There are two primary sources of mixed aromatics, catalytic reformate and stabilized pyrolysis gasoline. Coke oven light oil may also be processed. The C_5+ fraction of high octane reformate typically contains 45 to 70 volume percent aromatics, some normal and isoparaffins, small quantities of naphthenes and less than one percent olefins. Sulfur and nitrogen are removed in reforming. Table 30 describes a typical aromatics content in reformate.

The aromatic content of pyrolysis gasoline is described in Tables 26 and 27 in Process No. 15.

Solvents employed in the Udex process are di-, tri-, and tetra-ethylene glycols mixed with 8 to 12% water. Tetrahydrothiophenedioxide, $(CH_2)_4SO_2$, is the solvent in the Sulfolane process. Other processes employ dimethyl sulfoxide, diglycolamine, or N-methylpyrrolidone. Solvent to feed weight ratios for treating reformate are 20:1 for diethylene glycol and 7:1 for Sulfolane. Solvent to feed ratios increase with higher aromatic content of feed. Solvent makeup rates are 30 kg/Gg feed for the Sulfolane process and 0.9 g/m^3 feed (.03 lb/bbl feed) for the Udex process.

TABLE 30. TYPICAL AROMATICS CONTENT IN REFORMATE

Constituent	Volume % of Reformate
Benzene	5
Toluene	24
Ethylbenzene	4
Para-xylene	4
Meta-xylene	9
Ortho-xylene	5
C_9 and C_{10} aromatics	4
	55

Source: Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

3. Operating Parameters - Table 31 compares operating parameters for the Sulfolane and Udex processes. These data were based on an early Sulfolane process design, and more recently published data may be more accurate. Heat is supplied by steam for the Udex process and by direct-fired reboilers for the Sulfolane process described in this example.

Table 31. OPERATING PARAMETERS FOR UDEX AND SULFOLANE AROMATICS EXTRACTION PROCESSES

Operating Condition	Udex Process	Sulfolane Process
Stripping steam ratio, wt	.6	.13
Stripper bottom temperature, °C(°F)	140 (290)	190 (375)
Extractor top temperature, °C(°F)	140 (290)	100 (212)
Extractor pressure, kPa (psig)	860 (110)	207 (15)
Feed temperature, °C(°F)	115 (240)	115 (240)

Source: Deal, G. H., Jr., et al. "A Better Way to Extract Aromatics." Petroleum Refiner, September 1959, 195.

Process descriptions published in 1972 indicated that Udex unit capacities ranged from 30 to 4500 m^3/stream day (180 to 28,000 bbl/stream day), while Sulfolane unit capacities ranged from 50 to 7000 cm^3/stream day (300 to 45,000 bbl/stream day).

4. Utilities - Table 32 describes utility requirements for the same early Udex and Sulfolane processes described in Table 31.

Table 32. UTILITY REQUIREMENTS FOR UDEX AND SULFOLANE AROMATICS EXTRACTION PROCESSES

Utility Per Liter Feed (per bbl feed)	Udex Process	Sulfolane Process
Steam, kg (lb)	180 (400)	1.1 (2.5)
Fuel, MJ (10^3 Btu)	-	200 (190)
Cooling Water, m^3 (gal)	4.5 (1,200)	2.0 (530)
Electric Power, kWh	1.3	0.8

Source: Deal, G. H., Jr., et al. "A Better Way to Extract Aromatics." Petroleum Refiner, September 1959, 195.

A more recently published study indicates that solvent regeneration is done under vacuum. Steam requirements for one Sulfolane process design were around 286 kg/m^3 (100 lb/bbl) feed.

5. Waste Streams - Sources of waste streams include solvent regeneration, cooling water, and process leaks. Solvent regeneration is required due to formation of thermal degradation and polymerization products. The sludge produced in regeneration is disposed of by landfill. The production of vacuum for regeneration results in an oily waste stream.

Cooling water may be contaminated with aromatics due to heat exchanger leaks. One estimate indicated such leaks produced 50-200 ppm COD in cooling water.

Wastewater from the Udex process is reported to be produced at the rate of 0.504 m^3/Mg (60.4 gal/10^3 lb) of BTX extract produced. Total organic carbon in the wastewater is reported to be 0.144 kg/10^3 kg BTX extract produced.

The solvent makeup rates given in Section 2 indicate the amount of solvent that could appear in waste streams.

6. EPA Source Classification Code - None exists.

7. References -

(1) Bland, William F. and Robert L. Davidson, eds. Petroleum Processing Handbook. N.Y.: McGraw-Hill Book Company, 1967.

(2) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(3) Deal, G. H., Jr., et al. "A Better Way to Extract Aromatics." Petroleum Refiner, September 1959, 195

(4) Environmental Protection Agency (Office of Water and Hazardous Materials, Effluent Guidelines Div.). Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category. EPA 440/1-74-009-a. Washington, D. C.: 1974.

(5) Gloyna, E. F. and D. L. Ford. "The Characteristics and Pollutional Problems Associated with Petrochemical Wastes." Prepared for FWPCA Contract 14-12-461, Ada, Oklahoma: Robert S. Kerr Water Center, February 1970.

(6) Nelson, W. L. Petroleum Refinery Engineering. 4th ed. N.Y.: McGraw-Hill, 1958.

(7) "Refining Handbook." Hydrocarbon Processing, 51 (September 1972), 203-204.

(8) "Refining Handbook." Hydrocarbon Processing, 53 (September 1974), 192.

(9) Sittig, Marshall. Pollution Control in the Organic Chemical Industry. Park Ridge, N.J.: Noyes Data Corporation, 1974.

C_6-C_{9+} Aromatics Separation

1. Function - This process separates 99% pure mixed C_6-C_{9+} aromatic extract into pure benzene, toluene, mixed C_8 aromatics, and in some cases a C_{9+} fraction. Benzene is sold for use as a chemical intermediate. Toluene is used in fuels, as a chemical intermediate, or as a solvent. Part may be further processed in this industry to produce benzene or xylenes by dealkylation and disproportionation (Processes 22 and 23). The C_8 mixture is used for gasoline or solvent or further processed to separate the isomers (Processes 18 through 21).

The extract is first preheated and treated in clay towers for trace olefin and sulfur removal. Separation is accomplished in conventional overhead refluxed fractionation columns.

2. Input Materials - Aromatic extract produced as described in Process 16 is the input material. Relative proportions of the C_6, C_7, C_8, and C_9 fractions depend on the source of the extract. The aromatic content of pyrolysis gasoline is described in Process 15 and that of reformate in Process 16. Clay is also an input material. One process requires 0.6 kg of clay per m^3 (1 ton/10,000 barrels) of extract treated.

3. Operating Parameters - Information describing operating conditions was not found. Boiling points of the products are 78.8°C for benzene, 109.4°C for toluene, 137-142°C for the C_8 mixture, and 161-216°C for the C_{9+} fraction.

4. Utilities - Requirements include fuel or steam for preheating the extract and for the reboilers, cooling water for condensation, and power for pumping. Quantitative data were not found in the literature.

5. Waste Streams - Intermittent hydrocarbon emissions occur at relief vents. Fugitive hydrocarbon emissions may occur at valves and pump seals. Emissions from cooling water system operation and process heaters are discussed in the Industry Description.

Spent clay containing olefin polymerization products is discarded in one operation. Solid waste from this source amounts to 0.6 kg per m^3 extract treated (one ton of clay per 10,000 barrels of extract).

6. EPA Source Classification Code - None exists.

7. References -

(1) Bland, William F. and Robert L. Davidson, eds. Petroleum Processing Handbook. N.Y.: McGraw-Hill Book Company, 1967.

(2) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(3) Hedley, W. H., et al. Potential Pollutants From Petrochemical Processes. MRC-DA-406. Dayton, Ohio: Monsanto Research Corp., December 1973.

(4) Kerns, Gordon D. "Operating Cost Lowest in the Industry." Oil and Gas J., 58 (September 1960), 91.

(5) "Toluene," 696.5032 A. Chemical Economics Handbook. Menlo Park, California: Stanford Research Institute, 1972.

(6) "Xylenes," 699.5021 E. Chemical Economics Handbook. Menlo Park, California: Stanford Research Institute, 1971.

C_8 Aromatics Fractionation

1. Function - The purpose of this process is to separate ortho-xylene and ethylbenzene from C_8 aromatics mixtures. Both C_8 isomers are recovered for use as chemical intermediates. Separation is accomplished by fractional distillation for ortho-xylene and by superfractionation for ethylbenzene. Ortho-xylene is produced as the bottoms product of a 100- to 150-tray fractionation tower operated with a reflux ratio of 5-8 to 1. Ethylbenzene separation is more difficult and requires 350 to 400 trays with a reflux ratio of 25-50 to 1. A series of three columns may be employed. The remaining C_8 aromatics mixture is usually treated further for separation of other isomers. Depending on the feed material, this process may employ another step to separate ortho-xylene from C_9 and heavier aromatics.

2. Input Materials - Feed materials to this process are various mixtures of the aromatic C_8 isomers ethylbenzene, ortho-xylene, meta-xylene, and para-xylene. Sources of mixed C_8 aromatics include the C_{8+} fraction of extract from catalytic reformate or pyrolysis gasoline (Process 17), the equilibrium mixture from isomerization (Process 21), streams from other C_8 aromatic separation processes, and the product stream from toluene disproportionation (Process 22). The composition of C_8 isomers in input streams is shown in Table 33.

Table 33. TYPICAL COMPOSITION OF C_8 AROMATICS MIXTURES FROM VARIOUS SOURCES

Component	Catalytic Reformate	Pyrolysis Gasoline	Toluene Disproportionation
Ethylbenzene	21	53	-
Para-xylene	18	10	26
Meta-xylene	39	25	50
Ortho-xylene	22	12	24

Source: Atkins, R. S. "Which Process for Xylenes?" Hydrocarbon Processing, 49 (November 1970), 127-136.

3. Operating Parameters - Information describing operating conditions was not found. The boiling point of ethylbenzene is 136.2 °C, and that of ortho-xylene is 144.4 °C. Typical plant sizes are in the range of 45-90 Gg/year. (100-200 $X10^6$ pounds per year).

4. Utilities - Requirements include steam or fuel for reboilers, cooling water for condensers, and power for pumping. Consumption rates were not found in the literature. One source indicated that utilities for ethylbenzene superfractionation are prohibitively expensive at some locations.

5. Waste Streams - Intermittent hydrocarbon emissions occur at relief vents. Fugitive hydrocarbon emissions may occur at valves and pump seals. Emissions from cooling water system operation are discussed in the Industry Description.

6. EPA Source Classification Code - None exists.

7. References -

(1) Atkins, R. S. "Which Process for Xylenes?" Hydrocarbon Processing 49 (November 1970), 127-136.

(2) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(3) Hahn, Albert V. The Petrochemical Industry, Market and Economics. N.Y.: McGraw-Hill Book Company, 1970.

(4) Stobaugh, Robert B. "Xylenes: How, Where, Who--Future." Hydrocarbon Processing, 45 (April 1966), 149.

Para-Xylene Crystallization

1. Function - This process separates 99+% pure para-xylene from other aromatic isomers by fractional crystallization. Recovery of para-xylene is limited to about 60% due to formation of eutectics with ortho- and meta-xylene. A number of processes are available, and most include the following steps:

   1) Drying - Feedstock water content must be reduced to about 10 ppm. Drying is done in alumina or silica gel beds. Dual bed operation is practiced. Regeneration is accomplished with electric heaters or jacketed steam. Distillation is an alternative drying procedure.

   2) Crystallization - Two crystallization stages are employed in most processes. First-stage crystals are remelted and recrystallized. Scraped surface tubular exchangers or tank crystallizers are used.

   3) Cooling - First-stage crystallizer feed is partially cooled by heat exchange with filtrate from the second-stage crystallizer. Indirect refrigeration is usually employed. Propane, ethylene, propylene, ammonia, or a fluorocarbon are common refrigerants. One process employs direct refrigeration with an immiscible coolant.

   4) Solid-Liquid Separation - Continuous-solid bowl centrifuges or rotary drum suction filters are employed in most modern plants. Second-stage filtrate is recycled to the first-stage crystallizer. First-stage crystallizer mother liquor is a product stream which is treated by isomerization or fractionation to separate other C_8 isomers.

2. Input Materials - Feed materials to this process are the same as those to fractionation (Process 18). Crystallization processes which treat C_8 fractions of unextracted reformate may be available, but it is not evident whether such plants are operating in the U.S. Since only two-thirds of the para-xylene present can be recovered by crystallization, about 0.1-0.15 kg of para-xylene is produced per kg of typical mixed xylenes containing 12 to 22% para-xylene.

3. Operating Parameters - The first-stage crystallizer operates in the temperature range -60 to -70 °C (-80 to -90°F). Second-stage crystallizer temperature is -32 °C (-25°F). Significant operating parameters for the centrifuge are bowl revolution speed, bowl differential, and slurry pool depth. Values for these parameters were not found in the literature.

4. Utilities - Utility requirements for a 45 Gg/year (50,000 ton/yr) para-xylene crystallization facility are given in Table 34.

Table 34. UTILITY REQUIREMENTS FOR PARA-XYLENE CRYSTALLIZATION

Utility	Consumption Per Mg of Para-Xylene
Electric power, kWh	380
Steam, kg (ton)	230 (0.25)
Cooling water, m^3(gal)	100 (26,500)

Source: "Xylene Isomers Separated by New Process." Oil and Gas Journal, 15 December 1969, 82.

5. Waste Streams - Little information was found in the literature describing waste stream origin, volume, or composition. Waste streams probably originate from regeneration of dessicant, from refrigerant and pump seal leaks, and from refrigeration and cooling water system operations. Cooling is apparently the only water use in the process. One reference states that crystallization and accumulated wastes from drains or bottoms produce sludge in the amount of 0.4 to 2 m^3/Mg of product (100 to 500 gallons/ton of product). Since crystallizer mother liquor is recirculated, it is not clear how the sludge is produced. The sludge is said to contain 3-5,000 g/m^3 of organics. Wastes from cooling water and refrigeration system operations are discussed in the Industry Description.

6. EPA Source Classification Code - None exists.

7. References-

(1) Aalund, Leo R. "Xylene Boom Spawning New Processes." Oil and gas J., 27 November 1967,48.

(2) Atkins, R. S. "Which Process for Xylenes?" Hydrocarbon Processing, 49 (November 1970), 127-136.

(3) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(4) Desiderio, R. J. "Single-Stage Crystallization Can Cut Paraxylene Production Cost." Oil and Gas J., 8 July 1974, 116-117.

(5) Gloyna, E. F. and D. L. Ford. "The Characteristics and Pollutional Problems Associated with Petrochemical Wastes." Prepared for FWPCA Contract 14-12-461, Ada, Oklahoma: Robert S. Kerr Water Research Center, February 1970.

(6) Hahn, Albert V. The Petrochemical Industry, Market and Economics. N.Y.: McGraw-Hill Book Company, 1970.

(7) "Petrochemical Handbook." Hydrocarbon Processing, 52 (November 1973), 195.

(8) Stobaugh, Robert B. "Xylenes: How, Where, Who--Future." Hydrocarbon Processing, 45 (April 1966), 149.

(9) "Xylene Isomers Separated by New Process." Oil and Gas J., 15 December 1969. 82.

(10) "Xylenes," 699.5021 E. Chemical Economics Handbook. Menlo Park, California: Stanford Research Institute, 1971.

Para-Xylene Adsorption

1. Function - Para-xylene is separated from a mixture of C_8 aromatic isomers by selective adsorption in a fixed bed of porous solid adsorbent. In the Parex process the adsorbed para-xylene is desorbed by washing with a hydrocarbon of boiling point different from those of the aromatics. Raffinate and para-xylene are separated from the desorbent by fractionation. Equipment includes a single bed of adsorbent with a multiport rotary distributing valve. The arrangement simulates countercurrent flow of adsorbent and liquid without solid conveyance.

2. Input Materials - This process treats the same mixed xylene streams as the fractionation and crystallization processes (Processes 18 and 19). The unextracted C_8 fraction of reformate is also treated effectively in this process. Solid adsorbent and liquid desorbent makeup requirements were not found in the literature. Para-xylene recovery efficiencies of 95 to 99% are reported. At 95% recovery, assuming 20% para-xylene in the mixed xylene feed, 5.25 kg feed would be required per kg para-xylene produced.

3. Operating Parameters - The adsorption temperature is in the range of 120 to 150°C (250 to 300°F). Moderate pressures are employed. Operating conditions for fractionation were not found.

4. Utilities - Data have been published for the Japanese Aromax process which differs from the Parex process in the type of valve employed to simulate countercurrent flow of solid and liquid. Table 35 summarizes utility requirements for a combined Aromax adsorption-isomerization process. (Isomerization is described in Process 21.) The process treats 116 Gg/year of mixed xylenes and produces 100 Gg/year of para-xylene.

Table 35. UTILITY REQUIREMENTS FOR COMBINED ADSORPTION (AROMAX PROCESS) AND ISOMERIZATION PROCESS PRODUCING 100 Gg/YEAR PARA-XYLENE

Utility	Consumption Rate
Steam	12 Mg/hr
Absorbed Heat Duty	230 GJ/hr
Electric Power	3,900 kW
Cooling Water	136 Mg/hr

Source: "Petrochemical Handbook." Hydrocarbon Processing, 52 (November 1973), 196.

5. Waste Streams - Very little information was found in the literature describing this relatively new process. Blowdown from regeneration of adsorbent and desorbent and hydrocarbon leaks from vents, valves, and pump seals are possible sources of waste streams. Waste streams resulting from operation of cooling water and power and steam generation systems are discussed in the Industry Description.

6. EPA Souce Classification Code - None exists.

7. References -

(1) Atkins, R. S. "Which Process for Xylenes?" Hydrocarbon Processing, 49 (November 1970), 127-136.

(2) Brownstein, Arthur M., ed. U.. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(3) Otani, Seiya. "Adsorption Separates Xylenes." Chemical Engineering, 80 (September 1973), 106-107.

(4) "Petrochemical Handbook." Hydrocarbon Processing, 52 (November 1973), 196.

(5) "Petrochemical Handbook." Hydrocarbon Processing, 52 (November 1973), 198.

C_8 Aromatics Isomerization

1. Function - This process changes the composition of mixtures of C_8 aromatic isomers to the equilibrium composition at the operating conditions. The process is used to treat mixtures from which one or more of the isomers have been removed as described in Processes 18, 19, and 20. Isomerization is generally employed to convert the naturally most abundant meta-xylene isomer to ortho- and para-xylene, which are more widely used as chemical intermediates. Isomerization processes also convert some of the ethylbenzene to xylenes or to benzene and toluene by disproportionation.

A number of isomerization processes are offered. They differ primarily in the type of catalyst employed and in the resulting isomerization reactor operating conditions. Processing steps include the following:

- Feed is preheated by exchange with reactor effluent and further heated in a fired heater. Some processes employ hydrogen which is mixed with feed liquor after preheating.
- Isomerization occurs over a fixed bed of catalyst with hydrogen or steam.
- Gaseous and liquid isomerization products are separated in a flash drum. The hydrogen-rich gas stream is recycled to the reactor in processes which employ hydrogen. A purge gas stream is used to maintain hydrogen purity.
- Liquid isomerizate is fractionated, and benzene and tolune are recovered overhead. A fuel gas may be separated when light aromatics are condensed. Bottoms are fractionated in a rerun column which produces a C_9+ bottoms stream and the equilibrium xylene mixture for further treatment. By-products from this process include the C_9+ heavy aromatics fraction which may be input to toluene transalkylation (Process 22), some benzene and toluene, and a mixed-xylene solvent slip stream.

2. Input Materials - The feedstock, a mixture of C_8 isomers, usually contains a high proportion of meta-xylene and ethylbenzene and unrecovered amounts of ortho and para isomers. Mother liquor from para-xylene crystallization or adsorption, or overhead product from ortho-xylene fractionation are used. One Japanese process extracts meta-xylene with HF_3-BF_3 and employs the extract as feed to isomerization. Hydrogen is also an input material. Concentration in the feed can be as high as a 10 to 1 mole ratio.

3. Operating Parameters - Table 36 summarizes operating parameters for a number of isomerization processes. Not all of the processes listed in Table 36 are commercialized in the United States. Isomerization reactor size and yield depends on the amount of ethylbenzene in the feedstock and on the catalyst employed.

Table 36. OPERATING CONDITIONS FOR COMMERCIAL C_8 AROMATICS ISOMERIZATION PROCESSES

Licensor	Temperature °C	°F	Pressure kPa	Atm	Catalyst
Atlantic Richfield			100	1	Nonnoble metal
Engelhard, Octafining	400-500	800-900	>1000	>10	Platinum, requires hydrogen
ESSO, Isoforming	370-450	700-850	>1000	>10	Nonnoble metal, requires hydrogen
Imperial Chemical Industries	400-500	750-930	100	1	Nonnoble metal
Japan Gas, HF_3-BF_3 Extraction Isomerization	-1 to 10 66-93	30-50 150-200	100	1	HF_3-BF_3
Maruzen, XIS	460-560	860-1040	100	1	Silica-Alumina
U.O.P., Isomar	Moderate Conditions				Noble metal, requires hydrogen
Mobil, LTI	200-300	400-500	2000	20 psig	Zeolite, requires toluene diluent

Sources: Atkins, R. S. "Which Process for Xylenes?" Hydrocarbon Processing, 49 (November 1970), 127-136

Grandio, P. and F. H. Schneider. "AP-Catalyst Processes Make Aromatics at Low Temperature." Oil and Gas J., 29 November 1971, 62.

"Petrochemical Handbook." Hydrocarbon Processing, 52 (November 1973), 195

4. Utilities - Table 37 gives utility requirements for a combined process employing para-xylene crystallization and isomerization by the process licensed by Maruzen Oil Company. Isomerization is accomplished using silica-alumina catalyst with addition of steam at atmospheric pressure. Utilities for a combined adsorption-isomerization process are given in Process 20.

Table 37. UTILITY REQUIREMENTS FOR COMBINED XYLENE CRYSTALLIZATION-ISOMERIZATION PROCESS

Utility	Consumption Per Mg of Para-Xylene Produced
Steam	160 kg
Electricity	463 kWh
Cooling Water	98 Mg
Fuel Oil	16 GJ

Source: "Petrochemical Handbook." Hydrocarbon Processing, 52 (November 1973), 195.

5. Waste Stream - Two gas streams are produced by isomerization processes. Indications are that both the purge from the recycle hydrogen stream from the flash drum and the vent gas produced during separation and condensation of light aromatics are used as fuel gas.

Although no information was found describing waste streams in the literature consulted for this study, it is probable that they arise from periodic catalyst regeneration; disposal of spent catalyst; leaks at valves, vents, and pump seals; and operation of cooling water, steam generation, and power generation systems. The latter category is discussed in the Industry Description. Catalyst regeneration is accomplished by steam-air decoking in one process.

6. EPA Source Classification Code - None exists.

7. References -

(1) Aalund, Leo R. "Xylene Boom Spawning New Processes." Oil and Gas J., 27 November 1967, 48.

(2) Atkins, R. S. "Which Process for Xylenes?" Hydrocarbon Processing, 49 (November 1970), 127-136.

(3) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(4) Grandio, P. and F. H. Schneider. "AP-Catalyst Processes Make Aromatics at Low Temperature." Oil and Gas J., 29 November 1971, 62.

(5) Hedley, W. H., et al. Potential Pollutants From Petrochemical Processes. MRC-DA-406. Dayton, Ohio: Monsanto Research Corp., December 1973.

(6) "Petrochemical Handbook." Hydrocarbon Processing, 52 (November 1973), 195, 196.

(7) "Petrochemical Handbook." Hydrocarbon Processing, 54 (November 1975), 197.

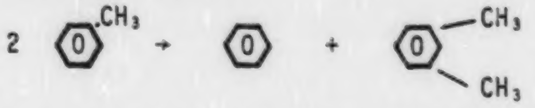
(8) Stobaugh, Robert B. "Xylenes: How, Where, Who--Future." Hydrocarbon Processing, 45 (April 1966), 149.

(9) "Xylenes," 699.5021 E. Chemical Economics Handbook. Menlo Park, California: Stanford Research Institute, 1971.

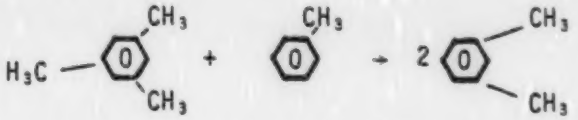
BTX PRODUCTION PROCESS NO. 22

Tolune Disproportionation/Transalkylation

1. Function - This vapor-or liquid-phase catalytic process converts toluene (C_7) to a mixture of xylene isomers (C_8) and benzene by the following disproportionation reaction:



If C_9 aromatics are present in the feed, they are also converted to xylenes by a transalkylation reaction:



Three processes are offered. Tatoray (U.O.P - Toray Industries) and Xylenes Plus (Atlantic Richfield) are vapor-phase processes and LTD (Low Temperature Disproportionation, Mobil) is a liquid-phase process.

Common processing steps include feed preheat, both by exchange with reactor effluent and in a fired heater; catalytic isomerization; and distillation to separate by-products. Hydrogen is used in the Tatoray process and toluene diluent is employed in the LTD process. Both are separated from product streams and recycled.

Separated by-product streams include a C_9 fraction which may be recycled; heavy ends including biphenyl and parts per million quantities of cyclic nonaromatics; light ends including benzene, light paraffins, and olefins produced by cracking; high purity benzene; and the mixed xylene stream which is input to xylenes separation processes 18, 19, or 20.

2. Input Materials - Input materials are extracted toluene, which may contain low concentrations of saturates, from Process 16 and C_9 aromatics. Hydrogen consumption in the Tatoray process is 4 kg per 1000 kg feed. This process can be operated to produce 414 kg benzene and 561 kg xylenes for each 1000 kg toluene feed. Table 38 illustrates how product ratios depend on C_9 content of feed.

3. Operating Parameters - The liquid-phase reaction takes place at 260 to 315°C (500 to 600°F) and 4.6 MPa (650 psig). Vapor-phase reactions are conducted at 370 to 540°C (700 to 1000°F). Vapor-phase process catalysts are nonprecious metals, while the catalyst for the liquid-phase process is a zeolite.

4. Utilities - Table 39 gives utility requirements for a 100 Gg/year facility with a product xylene to benzene ratio of 1.

Table 38. VARIATIONS OF DISPROPORTIONATION/TRANSALKYLATION PRODUCT RATIOS WITH C_9 CONTENT OF FEED

	Products		
Feed Composition	Benzene	Xylenes	Xylene/ Benzene
100% toluene	37%	55%	1.5
67% toluene 33% C_9 aromatics	13%	62%	6.2
50% toluene 50% C_9 aromatics	9%	87%	10

Source: Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

Table 39. UTILITY REQUIREMENTS FOR VAPOR PHASE CATALYTIC TOLUENE DISPROPORTIONATION WITH C_9 RECYCLE

Utility	Consumption per Mg Toluene Feed
Electric Power	73 kWh
Steam	1400 kg
Cooling water (Δt = 10°C)	2400 kg
Fuel	30 MJ

Source: "Petrochemical Handbook." Hydrocarbon Processing, 50 (November 1971), 133.

5. Waste Streams - Waste streams result from leaks at valves and pump seals; periodic catalyst regeneration; disposal of spent catalyst; process heaters; and operation of cooling water, steam and power generation systems. Emissions from the latter category are discussed in the Industry Description.

Two hydrocarbon waste streams are produced by disproportionation processes. A light ends off-gas stream containing paraffins and olefins is produced by the Tatoray process in the amount of 19 kg per 1000 kg feed. Heavy ends containing C_{10}+ aromatics such as biphenyl and cyclic nonaromatics are produced in quantities of about 10 kg per 1000 kg feed. For the liquid phase disproportionation process, the products include about 0.5% C_{10}+ hydrocarbons and 0.1% nonaromatics. These products may be ultimately disposed of as waste streams.

6. EPS Source Classification Code - None exists.

7. References -

(1) Brownstein, Arthur M. ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(2) Grandio, P. and F. H. Schneider. "AP-Catalyst Processes Make Aromatics at Low Temperature." Oil and Gas J., 29 November 1971, 62.

(3) "Petrochemical Handbook." Hydrocarbon Processing, 50 (November 1971), 133.

(4) "Petrochemical Handbook." Hydrocarbon Processing, 54 (November 1975), 115.

(5) "Xylenes," 699.5021 E. Chemical Economics Handbook. Menlo Park, California: Stanford Research Institute, 1971.

Hydrodealkylation

1. Function - Benzene is produced from toluene by catalytic or thermal dealkylation, as shown in the following reaction:

$$C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4$$

Excess hydrogen is added to prevent coking and cold hydrogen is employed as a quench for the highly exothermic reaction. Xylenes or other alkylaromatics may also be dealkylated to benzene by this process, but increased polymer and coke formation become problems.

Catalytic processes include the Hydeal (U.O.P.) and Detol (Houdry) processes. The HDA process (Atlantic Richfield - HRI) and the THD process (Gulf) are thermal processes. Common processing steps in producing benzene from toluene are described as follows:

Reactor feed and compressed recycle and makeup hydrogen are preheated by exchange with process streams and in a fired heater. Dealkylation is accomplished in a fixed-bed catalytic or thermal reactor. Reactor effluent is cooled using a waste heat boiler in some process designs, by exchange with fresh feed, and in water-cooled exchangers.

Dealkylation product is treated in a flash drum where a recycle hydrogen-rich gas stream is separated. A fuel gas purge stream is withdrawn. Liquid from the separator is treated in a stabilizer where dissolved hydrocarbons with boiling points below that of benzene are separated. A fuel gas stream is produced in this step also. Benzene is separated from stabilizer liquid effluent by distillation. Benzene column bottoms are recirculated to the dealkylation reactor. Clay treating may be required as a purification step in processes which treat unrefined starting materials.

2. Input Materials - Toluene, or mixtures of toluene and xylenes, and hydrogen are input materials to this process. Hydrodealkylation can also be used to produce benzene directly from impure or unrefined hydrocarbon mixtures containing alkyl aromatics such as pyrolysis gasoline, unextracted reformate cuts, or coke oven light oil fractions. Process 25 describes naphthalene production by hydrodealkylation. Table 40 shows typical input stream compositions used as the basis for a description of utility requirements for the Houdry process.

A 100 percent efficient toluene conversion process would yield 84.7 weight percent or 83 volume percent benzene. One source reported that practical efficiencies are around 97 percent, so that about 80 weight percent of the feed is converted to benzene. Industry estimates from another source are that 1.22 to 1.28 volumes of toluene are consumed for each volume of benzene produced. Toluene content of the Udex grade feedstock is about 92 to 95 percent. In some cases an 85-90 percent toluene/10-15 percent xylenes mixture may be used. Hydrogen-toluene mole ratios of 8 to 1 employed.

Table 40. TYPICAL COMPOSITION OF FEEDSTOCKS FOR HOUDRY HYDRODEALKYLATION PROCESS

	Feedstock		
Component (Percent)	Toluene	C_6- C_9 Fraction of Products from Thermal Cracking	C_6-C_9 Fraction of Coke Oven Light Oil
C_{5+} Paraffins, Naphthenes, and olefins		32	3
Benzene		33	74
Toluene	100	14	15
C_8 Aromatics		13	4
Styrene		2	2
C_{9+} Aromatics		6	2

Source: Chemical Engineering, ed. Sources and Production Economics of Chemical Products, 1973-1974. 1st ed. N.Y.: McGraw-Hill, 1974.

3. Operating Parameters - Catalytic processes (Detol, Hydeal) typically operate at 540 to 650°C (1000 to 1200°F). Thermal processes (THD, Hydrodealkylation) are conducted at temperatures as high as 760°C (1400°F). Pressures in the range from 3.5 to 8.4 MPa (500-1200 psig) are employed in both processes. The catalyst employed in the Detol process is in the form of cylindrical pellets of unreported composition. A description of the catalyst used in the Hydeal process was not found in the literature.

4. Utilities - Table 41 shows estimated utility consumption for conversion of 160 m^3 (1000 bbl)/stream day of Udex grade toluene by a Hydeal process including a heater, a reactor, a recycle gas compressor, a hydrogen generator, clay treating, and product fractionation. Cooling water system, power generation, utilities distribution and waste disposal are not included. Table 42 summarizes utility requirements for the Houdry process based on the input compositions described in Table 40.

Table 41. UTILITY CONSUMPTION RATES FOR BENZENE PRODUCTION FROM TOLUENE BY THE HYDEAL PROCESS

	Utility	Consumption Rate	
(1.1 MPa)	Steam, kg/hr (lb/hr)	2900	(6300)
(4.2 MPa)	Steam, kg/hr (lb/hr)	1400	(3000)
	Fuel, GJ/hr (Btu/hr)	13.2	(12.5 x 10^6)
	Electricity, kW	800	
	Cooling Water, dm^3/s (gal/min)	0.789	(12.50)

Source: Asselin, G. F. and R. A. Erickson. "Benzene and Naphthalene from Petroleum by the Hydeal Process." Chemical Engineering Progress, 58 (April 1962), 47.

Table 42. UTILITY REQUIREMENTS FOR THE HOUDRY CATALYTIC HYDRODEALKYLATION PROCESS

	Quantity Required Per Mg Benzene Produced From		
Utility	Toluene	Pyrolysis Gasoline	Coke Oven Light Oil
Electric Power, GJ (kWh)	0.194 (54.0)	0.187 (52.0)	0.163 (45.2)
Steam Consumed, kg	44	970	150
Steam Produced, kg	-	905	537
Net Steam, kg	-44	-65	+387
Boiler Feedwater, kg	-	3	16.3
Cooling Water, kg	16,900	43,500	28,600
Fuel Consumed, GJ (10^6 Btu)	2.63 (2.49)	3.49 (3.30)	3.91 (3.70)
Fuel Produced, GJ (10^6 Btu)	11.6 (11.0)	29.1 (27.5)	5.70 (5.40)
Net Fuel, GJ (10^6 Btu)	+9.00 (8.52)	+25.4 (24.0)	+1.79 (1.69)

Source: Chemical Engineering, ed. Sources and Production Economics of Chemical Products, 1973-1974. 1st ed. N.Y.: McGraw-Hill, 1974.

5. Waste Streams - Little information was found in the literature describing waste streams. It is probable that waste streams originate from periodic catalyst regenerating; fugitive emissions from valves and pump seals; discarding spent clay; and operating power generation and cooling water systems, gas compressors, and process heaters. These systems are discussed in the Industry Description.

Catalyst regeneration in the Detol process involves occasional burning of coke deposits in a preheated inert gas with controlled quantities of air. Descriptions of the Hydeal process indicate that about one percent of aromatics in the feed may be converted to heavy aromatics such as biphenyl, methylbiphenyls and fluorene through condensation of aromatic nuclei. Ultimately, these heavy aromatics must be found in waste streams.

6. EPA Source Classification Code - None exists.

7. References -

(1) Asselin, G. F. and R. A. Erickson. "Benzene and Naphthalene from Petroleum by the Hydeal Process." Chemical Engineering Progress, 58 (April 1962), 47.

(2) Brownstein, Arthur M., ed. U.S. Petrochemicals, Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(3) Chemical Engineering, ed. Sources and Production Economics of Chemical Products, 1973-1974. 1st ed. N.Y.: McGraw-Hill, 1974.

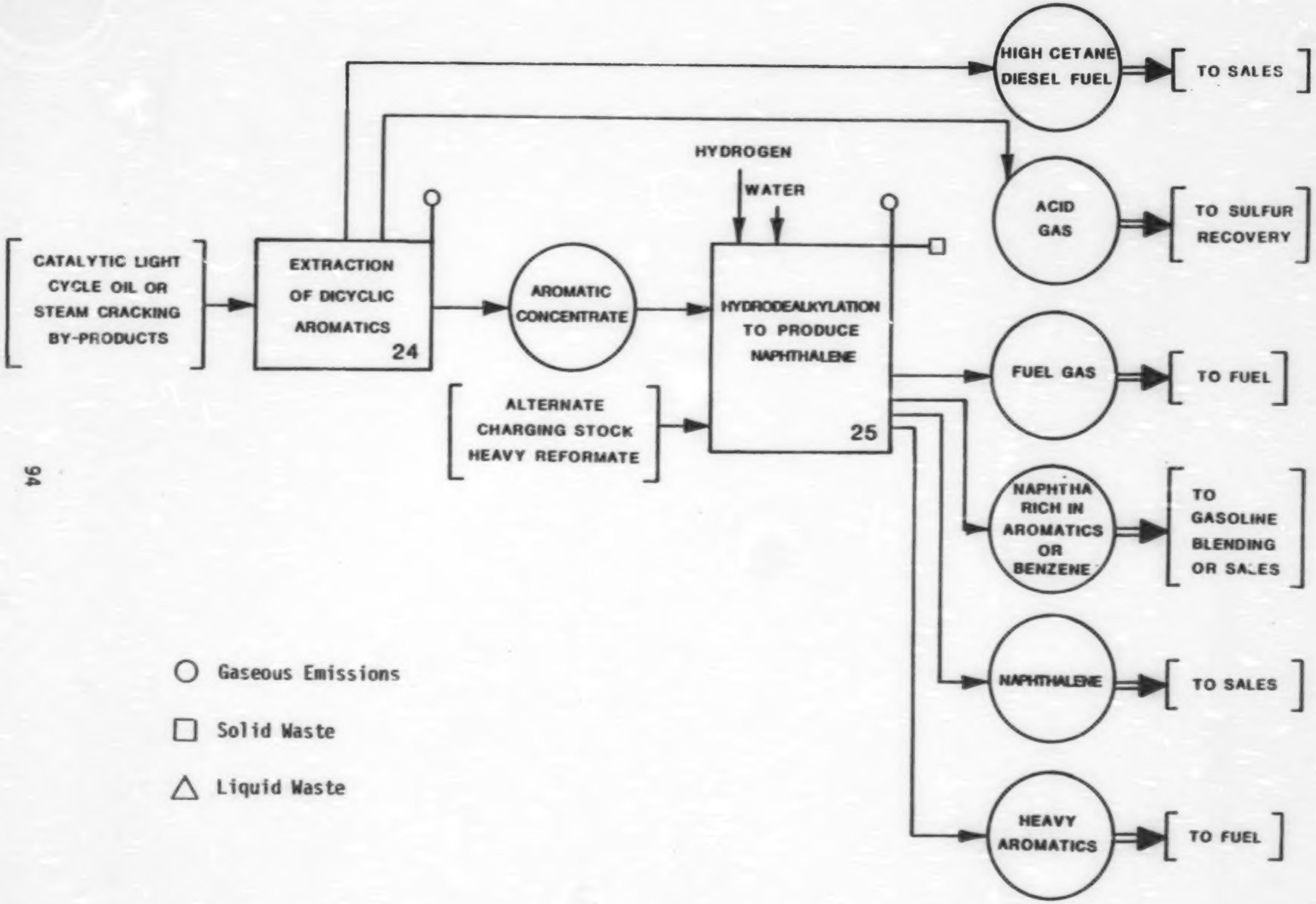
(4) Erskine, Mimi G. "Benzene." 618.5021 A. Chemical Economics Handbook. Menlo Park, California: Stanford Research Institute, 1972.

(5) Petroleum Refiner, 40 (November 1961), 236, 251, 252, 298.

NAPHTHALENE PRODUCTION PROCESSES

This operation of the basic petrochemical industry produces naphthalene from heavy reformate, catalytic cycle oils, or by-products from steam cracking to produce olefins. Although naphthalene is also produced from coal tar, this treatment is restricted to production from petroleum sources.

Figure 8 shows the required processes which include aromatics extraction for those feeds with relatively low aromatics content (Process No. 24) and dealkylation of alkyl naphthalenes (Process No. 25). The major by-product is an aromatics-rich naphtha which may be used in blending gasolines or from which benzene may be separated.



CATALYTIC LIGHT CYCLE OIL OR STEAM CRACKING BY-PRODUCTS
EXTRACTION OF DICYCLIC AROMATICS
24
AROMATIC CONCENTRATE
ALTERNATE CHARGING STOCK HEAVY REFORMATE
HYDROGEN
WATER
HYDRODEALKYLATION TO PRODUCE NAPHTHALENE
25
HIGH CETANE DIESEL FUEL
TO SALES
ACID GAS
TO SULFUR RECOVERY
FUEL GAS
TO FUEL
NAPHTHA RICH IN AROMATICS OR BENZENE
TO GASOLINE BLENDING OR SALES
NAPHTHALENE
TO SALES
HEAVY AROMATICS
TO FUEL
○ Gaseous Emissions
□ Solid Waste
△ Liquid Waste

Figure 8. NAPHTHALENE PRODUCTION PROCESSES

Extraction of Dicyclic Aromatics

1. Function - Dicyclic (and higher) aromatic compounds are extracted from catalytic gas oil or other materials of similar composition. The aromatic rich product is dealkylated to produce naphthalene and the dearomatized product is a high cetane number diesel fuel.

Dicyclic aromatics are selectively adsorbed from the liquid phase onto fixed beds of adsorbent (silica gel). Desorption is effected by elution with solvent with a boiling range different from that of the desired product. Product and desorbent are separated by fractional distillation. Some sources indicate that removal of water and compounds containing nitrogen, sulfur or oxygen is required before the extraction step. Other sources indicate hydrodesulfurization of the aromatic extract after separation.

Hydrodesulfurization and Acid Gas Removal are described as Processes No. 4 and 16 in the Petroleum Refining Industry Chapter of this catalog.

2. Input Materials - The process is designed to extract aromatics from a complex mixture. The extraction technique is flexible and different relative amounts of dicyclic and monocyclic aromatics can be extracted from a given feed by varying the nature of the adsorbent used and the operating conditions. One source indicates stream compositions listed in the table below for a catalytic gas oil (bp 226-268°C) feed and for the product streams derived from it.

Table 43. STREAM COMPOSITIONS FOR EXTRACTION PROCESS

	Composition of Streams (weight percent)		
Compound Type	Catalytic Gas Oil Feed bp 226-268°C	Aromatic Extract	Lean Stream
Total Aromatics	53.7	100	25.8
Dicyclic Aromatics	25.7	62	4.0
Monocyclic Aromatics	28.0	38	21.8

Source: Barbor, R. P. "Naphthalene from Catalytic Gas Oil." Oil and Gas J., 21 May 1962, 123.

3. Operating Parameters - Temperatures do not exceed the atmospheric bubble points of the charge stocks. Pressures are moderate, basically those required to pump the feed through the adsorbent beds, and generally do not exceed 1.4 MPa (200 psi). The commercial installation described in the literature is designed to provide feed for a plant capable of producing 68 Gg (150×10^6 pounds) of naphthalene per year. Each kilogram of aromatic extract yields 0.4 kilogram of naphthalene, so 170 Gg of aromatic extract would be required to operate the

naphthalene plant at full capacity. The naphthalene plant can operate on other feeds which do not require aromatic extraction so the actual capacity of the aromatic extraction complex is probably somewhat below the figure cited.

4. Utilities - No information was available which gave utility requirements for aromatic extraction of alkyl naphthalenes directly. One source gave utility requirements for processing both heavy reformate and a catalytic cycle stock containing 14.6% by weight dicyclic aromatics. The difference between the utility requirement for the two stocks is in feed pretreatment which includes aromatic extraction, hydrodesulfurization and acid gas removal. The values given are listed in the table below on a per kilogram naphthalene produced basis. The difference should be taken as a very crude estimate of an upper limit for utility requirements.

Table 44. UTILITY REQUIREMENTS FOR EXTRACTION OF ALKYL NAPHTHALENES FROM DIFFERENT STOCKS

	Utility Requirements For:		
	Catalytic Cycle Stock Per kg Naphthalene	Heavy Reformate Per kg Naphthalene	Difference Per kg Naphthalene
Electric Power	8.2 watts	5.5 watts	2.7 watts
Fuel	29.5 MJ	13.1 MJ	16.4 MJ
Steam	zero	0.56 kg	not calculated
Circulating Water	106 liters	63 liters	43 liters

Source: "Hydrodealkylation Processes." Industrial and Engineering Chemistry, 54 (February 1962), 28-33.

5. Waste Streams - Available process descriptions do not address the subject of waste streams; however, several observations can be made.

Emissions of hydrocarbons to the atmosphere can be expected from vents of distillation units and from fugitive sources such as pump seals and flanges. Atmospheric emissions from process heaters are described as Process 31 for the Petroleum Refining Industry. Waste streams resulting from cooling water treatment are discussed in the Industry Description. Costs for chemicals are listed in economic descriptions of these processes but the process descriptions give little information as to the type of chemicals or their fate. Waste from acid gas removal are discussed in Chapter 3, The Refining Industry, and in Process No. 5 of this entry.

Spent sorbent represents a solid waste material, presumably to be disposed of by landfill. However, the sorbent is reported to have a long life so only a small amount of material is involved.

6. EPA Source Classification Code - None exists.

7. References -

(1) Barbor, R. P. "Naphthalene from Catalytic Gas Oil." Oil and Gas J., 21 May 1962, 123.

(2) Bland, William F. and Robert L. Davidson, eds. Petroleum Processing Handbook. N.Y.: McGraw-Hill Book Company, 1967.

(3) Broughton, D. B. and L. C. Hardison. "Unisorb Extracts Naphthalene Homologs.: Hydrocarbon Processing and Petroleum Refiner, 41 (May 1962), 125.

(4) "Hydrodealkylation Process." Industrial and Engineering Chemistry, 54 (February 1962), 28-33.

(5) Stanford Research Institute. 1975 Directory of Chemical Producers, U.S.A. Menlo Park, California: 1975.

Hydrodealkylation to Produce Naphthalene

1. Function - Feed materials rich in alkyl naphthalenes are dealkylated in the presence of hydrogen to produce naphthalene. In addition to high purity naphthalene the process yields fuel gas, a light naphtha high in benzene (or benzene), and a heavy component used for fuel. Hydrogen, and in some processes water, is required in addition to the charging stock. The process involves dealkylation, separation and product purification. Different processes differ in the order in which these process steps are carried out and in the specific types of separation and purification methods used. The charge may be fed directly to the dealkylation unit and the dealkylated product separated by fractional distillation. Alternatively, naphthalene may be separated from the charge by distillation before dealkylation. In the latter case the dealkylated product is recycled to the fractionating tower. Dealkylation may be carried out catalytically or noncatalytically (thermally). Other separations may be carried out in high-pressure separators or in low-pressure separators. Purification may involve sorption of impurities on acid treated clay, further fractionation, and/or fractional crystallization.

2. Input Materials - Charging stock, hydrogen and sometimes water are required input materials. Suitable charging stocks include catalytic reformate bottoms (bp 210-290°C 410-560°F), or aromatic extract from catalytic cycle oil (bp 226-268°C 440-515°F), or by-products from steam cracking operations in which olefins are made. Middle oil or crude naphthalene from coal tar may be partially refined by this process. Typical compositions presented in one source are given in Table 45 below.

Table 45. TYPICAL COMPOSITION OF NAPHTHALENE CHARGE STOCKS

	Catalytic Reformates	Catalytic Light Cycle Oil	Steam Cracking By-Products	Coal Tars
Total Aromatics (wt %)	90-95	45-65	70-95	95-100
Aromatics Composition (wt %)				
Alkylbenzenes	20	25	20	5
Indans and Tetralins	15	25	10	5
Indenes	2	7	18	3
Alkyl Naphthalenes	55	35	45	75
Biphenyls and Acenaphthenes	6	6	5	10
Tricyclics	2	2	2	2

Source: Asselin, G. F. and R. A. Erickson. "Benzene and Naphthalene from Petroleum by the Hydeal Process." Chemical Engineering Progress, 58 (April 1962), 47.

Other literature sources indicate that heavy catalytic reformates contain approximately 10% naphthalene in addition to 55% alkyl naphthalenes. In this case the percentage of other components would be reduced.

In general it will be economically advantageous to extract aromatics from a feed containing less than 70% aromatics before charging the feed to the dealkylation unit and economically disadvantageous to extract them from feeds containing 95% or more aromatics. The economics of aromatics extraction have to be studied on an individual basis for feeds in the range of 70-95% aromatics. Aromatics extraction (Process 24) is described earlier in this catalog entry.

Table 46 presents the product yields for the Hydeal Process (UOP) processing a heavy reformate feed which is 100% aromatics. Hydrogen makeup gas (90% by Volume H_2) requirements are 860 m^3/m^3 feed (4,815 scf/bbl feed).

Table 46. PRODUCT YIELDS FROM THE HYDEAL PROCESS

	Yield of Products Per m^3 Feed	Yield of Products Per Barrel Feed
Naphthalene	400 kg	140 lbs
Benzene	0.20 m^3	0.20 bbl
Heavy Product	0.04 m^3	0.04 bbl
Off-Gas	730 m^3(standard conditions)	4,105 scf
(Heating value 37 MG/m^3;		
1000 Btu/ft^3		

Source: Asselin, G.F. and R.A. Erickson. "Benzene and Naphthalene from Petroleum by the Hydeal Process." Chemical Engineering Progress, 58 (April 1962), 47.

3. Operating Parameters - The range of operating temperatures is 540-760°C (1000-1400°F), and operating pressures range from 3.5 to 7.0 MPa (500-1200 psig). Capacities of plants producing naphthalene from petroleum products range from 45 to 68 Gg per year (100-150x10^6 pounds/year). Some processes do not use catalysts; for those which do, it can be assumed that a catalyst of the same general type used for toluene dealkylation (nonoble metal compounds) is used.

4. Utilities - Utility requirements for the Hydeal Process using a heavy reformate (100% aromatic) feed to produce naphthalene are listed below in Table 47.

Table 47. UTILITY REQUIREMENTS FOR HYDEAL PROCESS

	Utility Required Per Kilogram Naphthalene Produced	Utility Required Per Pound Naphthalene Produced
Fuel	23.2 MJ	10,000 Btu
Electricity	0.47 KWh	0.21 KWh
Cooling Water	0.20 m^3	23 gallons

Source: Same as Table 46.

No steam requirements were listed for this process in the literature consulted, although high-pressure steam and low-pressure steam requirements were listed for the same process optimized for benzene production.

5. Waste Streams - Available process descriptions do not address the subject of waste streams; however, several observations can be made concerning potential problems.

Emissions of hydrocarbons to the atmosphere can be expected from distillation unit vents and from pump seals and flanges. For processes which use catalysts, catalyst decoking operations can be expected to release particulates, sulfur oxides and carbon monoxide to the atmosphere. Atmospheric emissions from process heaters are described in Process 31 for the Petroleum Refining Industry. Waste streams resulting from cooling water treatment are discussed in the Industry Description. Costs for chemicals are listed in economic descriptions of these processes but the process descriptions give no information as to the type of chemicals used or their fate.

Spent catalyst and acid treated clay used in purification form solid waste streams. Landfill is the usual method of disposal. The pH and heavy metal content of leachates from these materials would be of interest. The nature of the substances sorbed by the clay has not been of concern to developers of these processes. It is possible that some of the sorbed materials are toxic and could be mobilized to the environment by leaching of landfill. Benzene purification processes consume 0.0002 to 0.0004 kilograms clay per kilogram benzene purified.

6. EPA Source Classification Code - None exists.

7. References -

(1) Asselin, G. F. and R. A. Erickson. "Benzene and Naphthalene from Petroleum by the Hydeal Process." Chemical Engineering Progress, 58 (April 1962), 47.

(2) Barbor, R. P. "Naphthalene from Catalytic Gas Oil." Oil and Gas J., 21 May 1962, 123.

(3) Bland, William F. and Robert L. Davidson, eds. Petroleum Processing Handbook. N.Y.: McGraw-Hill Book Company, 1967.

(4) Brownstein, Arthur M., ed. U.S. Petrochemicals. Technologies, Markets, and Economics. Tulsa, Oklahoma: Petroleum Publishing Company, 1972.

(5) Chemical Engineering, ed. Sources and Production Economics of Chemical Products, 1973-1974. 1st ed. N.Y.: McGraw-Hill, 1974.

(6) Considine, Douglas M., ed. Chemical and Process Technology Encyclopedia. N.Y.: McGraw-Hill Book Company, 1974.

References (continued) -

(7) Erskine, Mimi G. "Naphthalene," 677.5020 G. Chemical Economics Handbook. Menlo Park, California: Stanford Research Institute, 1970.

(8) Hahn, Albert V. The Petrochemical Industry, Market and Economics. N.Y.: McGraw-Hill Book Company, 1970.

(9) Hawley, Gessner G. The Condensed Chemical Dictionary. 8th ed. Revised by G. G. Hawley. N.Y.: Van Nostrand Reinhold Co. (1971), 603.

(10) Hedley, W. H., et al. Potential Pollutants From Petrochemical Processes. MRC-DA-406. Dayton, Ohio: Monsanto Research Corp., December 1973.

(11) Industrial and Engineering Chemistry, 54 (February 1962), 28.

(12) Petroleum Refiner, 40 (November 1961), 236, 251-2, 298.

(13) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 8. 2nd ed. N.Y.: Interscience Publishers, 1965.

(14) Stanford Research Institute. 1975 Directory of Chemical Producers, U.S.A. Menlo Park, California: 1975.

(15) Stobaugh, Robert B. "Naphthalene: How, Where, Who--Future." Hydrocarbon Processing, 45 (March 1966), 149.

CRESOLS AND CRESLYIC ACIDS PRODUCTION PROCESSES

This operation includes the recovery of cresols and cresylic acids from refinery waste streams but does not include coal tar processing methods, even though most plants process both feedstocks. Also excluded from this discussion are synthetic methods of manufacture.

The operations are presented in two process descriptions: 26) Acidification and 27) Separation. Each process encompasses several processing steps, and the general processing scheme is illustrated in Figure 9. Quantitative information was not readily available for utilities and emissions. Qualitative descriptions are offered for waste stream information.

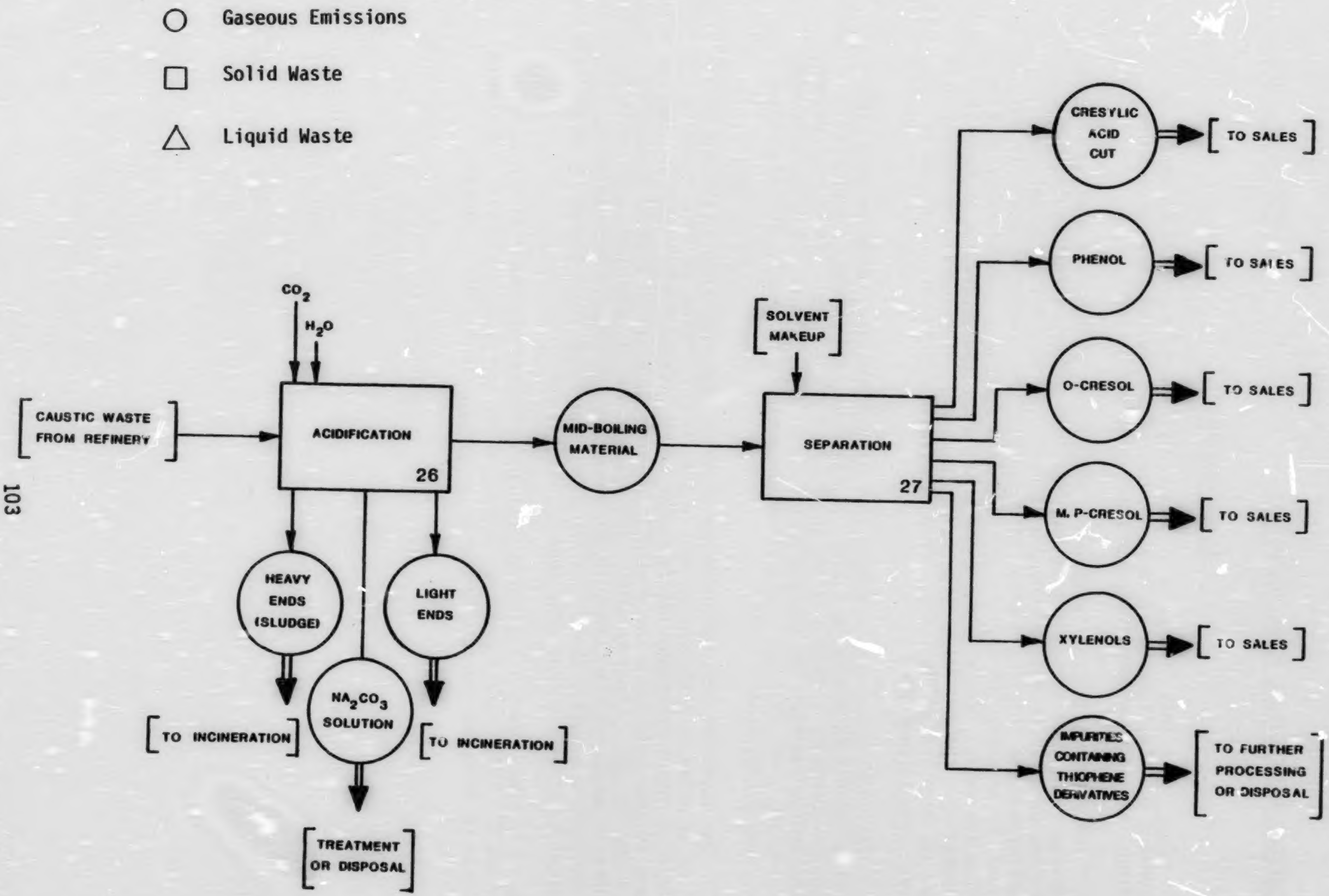

○ Gaseous Emissions
□ Solid Waste
△ Liquid Waste
CAUSTIC WASTE FROM REFINERY
CO2
H2O
ACIDIFICATION
26
HEAVY ENDS (SLUDGE)
TO INCINERATION
NA2CO3 SOLUTION
TREATMENT OR DISPOSAL
LIGHT ENDS
TO INCINERATION
MID-BOILING MATERIAL
SOLVENT MAKEUP
SEPARATION
27
CRESYLIC ACID CUT
TO SALES
PHENOL
TO SALES
O-CRESOL
TO SALES
M. P-CRESOL
TO SALES
XYLENOLS
TO SALES
IMPURITIES CONTAINING THIOPHENE DERIVATIVES
TO FURTHER PROCESSING OR DISPOSAL

Figure 9. CRESOLS AND CRESYLIC ACIDS PRODUCTION PROCESSES

Acidification

1. Function - This process acidifies caustic petroleum refinery wastes to convert the alkoxides to hydroxyl groups. There may be three processing steps involved: preparation, springing, and separation.

The preparation step is variable and depends on the feed and the process design. The feed stream may be devolatilized to remove the remaining hydrocarbon gases which may be vented or flared. In some installations the mercaptans and thiols are oxidized under alkaline conditions with air and steam to separate the sulfur compounds as disulfides. The products of this step are pumped into a settling tank from which the separation is made by decanting. The disulfide layer is incinerated. Other cresol recovery plants do not have preparation steps, using the raw refinery stream as feed to springing instead.

The prepared stream is pumped to a packed springing tower in which the actual acidification takes place. The aqueous feed stream is contacted countercurrently with CO_2, often in the form of flue gas. This step converts the sodium phenates and cresylates to phenol and cresols. To minimize cresol solubility, the flue gas composition is carefully controlled for an optimum carbonate-bicarbonate level.

The acids are decanted from the water in settling tanks. They may be further dried by distillation before they are fractionated. The phenolic layer enters a fractionation column in which light and heavy ends are removed and incinerated, while the mid-boiling range material is sent to processing in the solvent extraction unit. The aqueous sodium carbonate layer contains phenols whose concentrations may be reduced by absorption and stripping. Resultant wastewater contains phenols in quantities great enough to necessitate careful disposal and/or treatment.

2. Input Materials - Caustic waste from refineries is the feed stream to this process. This waste stream may contain 6-50% tar acids along with 10% thiols. Table 48 presents the composition of a typical spent caustic stream.

Table 48. TYPICAL COMPOSITION OF CAUSTIC STREAM FROM REFINERY

Compound		Composition (%)
Phenol		20
o-cresol		18
m-cresol		22
p-cresol		9
2,4-& 2,5-xylenols	25% —	8
3,4-xylenols		8
2,3-& 3,5-xylenols		12
Higher phenolics		3
Mercaptans		10
Sodium hydroxide		10
Napthenic acids		0.2
Carboxylic acids		0.2
Neutral oil		1.0
Water		54

Source: Chemical Engineering, 20 August 1962, 66.

Other required input materials are flue gas (8-14% CO_2) or CO_2, and air and/or steam for oxidizing the feed.

3. Operating Parameters - The fractionating column separates substances that distill below 100°C as light ends and substances boiling above 235°C as heavy ends.

On plant reports a bubble-cap column of 11 meters (35 ft) by 0.91 meters (3 ft) diameter for the separation step. The same plant utilized an 18 meter (60 ft) by 1.8 meter (6 ft) diameter springing tower packed with Raschig rings.

4. Utilities - Steam is required for oxidation and for reboiling; cooling water is required for condensing; energy is required for pumps.

5. Waste Streams - The aqueous solution resulting from springing has the potential for being a pollution problem. The phenol content of this stream may be as high as 2 to 6 % of the original feed concentration. Concentrations of some aqueous wastes from springing are presented in Table 49.

Table 49. PHENOL CONTENT OF AQUEOUS WASTES FROM EIGHT SPRINGING PROCESSES

Stream	Concentration of Phenols (ppm)
1	8,000
2	7,000
3	2,000
4	400
5	2,600
6	3,000 - 10,000
7	1500
8	12,000

Source: Beychok, Milton R. Aqueous Wastes from Petroleum and Petrochemical Plants. Great Britain: John Wiley & Sons, 1967.

If solvent extraction is used to recover phenols from this stream, the concentration may be reduced to 100 ppm. Biological treatment methods have been reported for further reducing phenol concentrations. One plant reports disposal of waste containing 100 ppm phenols in subsurface strata. Emissions from cooling water and steam generation systems are discussed in the Industry Description.

6. EPA Source Classification Code - None exists.

7. References -

(1) Beychok, Milton R. Aqueous Wastes from Petroleum and Petrochemical Plants. Great Britain: John Wiley & Sons, 1967.

(2) Chemical Engineering, July 1957, 228.

(3) Chemical Engineering, 20 August 1962, 66.

(4) Hahn, Alvert V. The Petrochemical Industry, Market and Economics. N.Y.: McGraw-Hill Book Company, 1970.

(5) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 6. 2nd ed. N.Y.: Interscience Publishers, 1965.

Product Recovery

1. Function - The tar acids from the acidification process (Process No. 26) are separated into marketable products in this process. Two processing steps are identified: solvent extraction and fractionation.

Solvent extraction is typically done with aqueous methanol and naphtha. The phenols are concentrated in the methanol layer, while the naphtha removes most of the impurities including thiophenols. The naphtha stream is stripped for recycle of the naphtha. Thiophenols and thiocresols may be recovered from the impurities, but in many instances the impurities are incinerated. The methanol stream is stripped before the phenolic stream is pumped to a separating tank where water is removed. The acid stream is then fed to a series of fractional distillation columns for separation of phenol, o-cresol, m-& p-cresol and mixed xylenols. A mixed cresylic acids cut may be taken. Cresylic acid product is defined as a mixture of cresols, xylenols, and phenols, 50% of which boil above 204°C. There may be an ion-exchange column present in this section of the plant to remove traces of mercaptans and bases from the phenolic compounds.

2. Input Materials - Typical tar acids contain 20% phenol, 18% o-cresol, 22% m-cresol, 9% p-cresol, 28% xylenols, and 3% higher phenolics. Makeup requirements for solvents are assumed to be low because of recycle techniques.

3. Operating Parameters - Pitt Consol's Newark plant utilizes an 18 meter (60 ft) by 0.9 meter (3 ft) diameter Scheibel extractor for the solvent extraction step. The methanol and naphtha flow countercurrently; the acid stream flows cocurrently with the methanol. The fractionation takes place in 0.9 meter (3 ft) diameter bubble-cap columns 18-23 meters (60 to 75 ft) tall. The settling tanks have a reported capacity of 30.3 m^3 (8000 gal).

Fractionation equipment for this process is usually of stainless steel or stainless-clad mild steel, as regular steel causes discoloration of product.

4. Utilities - Quantitative data are not readily available in the literature consulted. Steam and cooling water are required for fractionation columns. Energy for pumping various plant streams is required.

5. Waste Streams - Wastewater contaminated with phenolic compounds is generated from the aqueous methanol extraction. No information was found on the final disposition or treatment of this wastewater.

Fractionation columns are sources of intermittent and fugitive hydrocarbon emissions.

Incineration of impurities from the naphtha stream is a potential source of SO_x emissions.

Emissions from cooling water and steam generation systems are discussed in the Industry Description.

6. EPA Source Classification Code - None exists

7. References

(1) Beychok, Milton R. Aqueous Wastes from Petroleum and Petrochemical Plants. Great Britain: John Wiley & Sons, 1967.

(2) Chemical Engineering, July 1957, 228.

(3) Chemical Engineering, 20 August 1962, 66.

(4) Hahn, Albert V. The Petrochemical Industry, Market and Economics. N.Y.: McGraw-Hill Book Company, 1970.

(5) Standon, Anthony, ed. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 6. 2nd ed. N.Y.: Interscience Publishers, 1965.

NORMAL PARAFFIN PRODUCTION PROCESSES

In this operation normal paraffins are separated from branched and cyclic compounds. The separation is effected by sorption of the normal paraffins onto molecular sieves followed by recovery from the sieves. The boiling range of the normal paraffin product is determined by the boiling range of the feed material. Naphthas, kerosenes, or light gas-oils may be used as feeds. The most important applications of this process are to kerosenes and light gas-oils to produce normal paraffins which are used in the manufacture of biodegradable detergents. The literature contains descriptions of a urea process, but no commercial installations using this process are being operated in the United States.

The flowsheet in Figure 10 describes normal paraffin production.

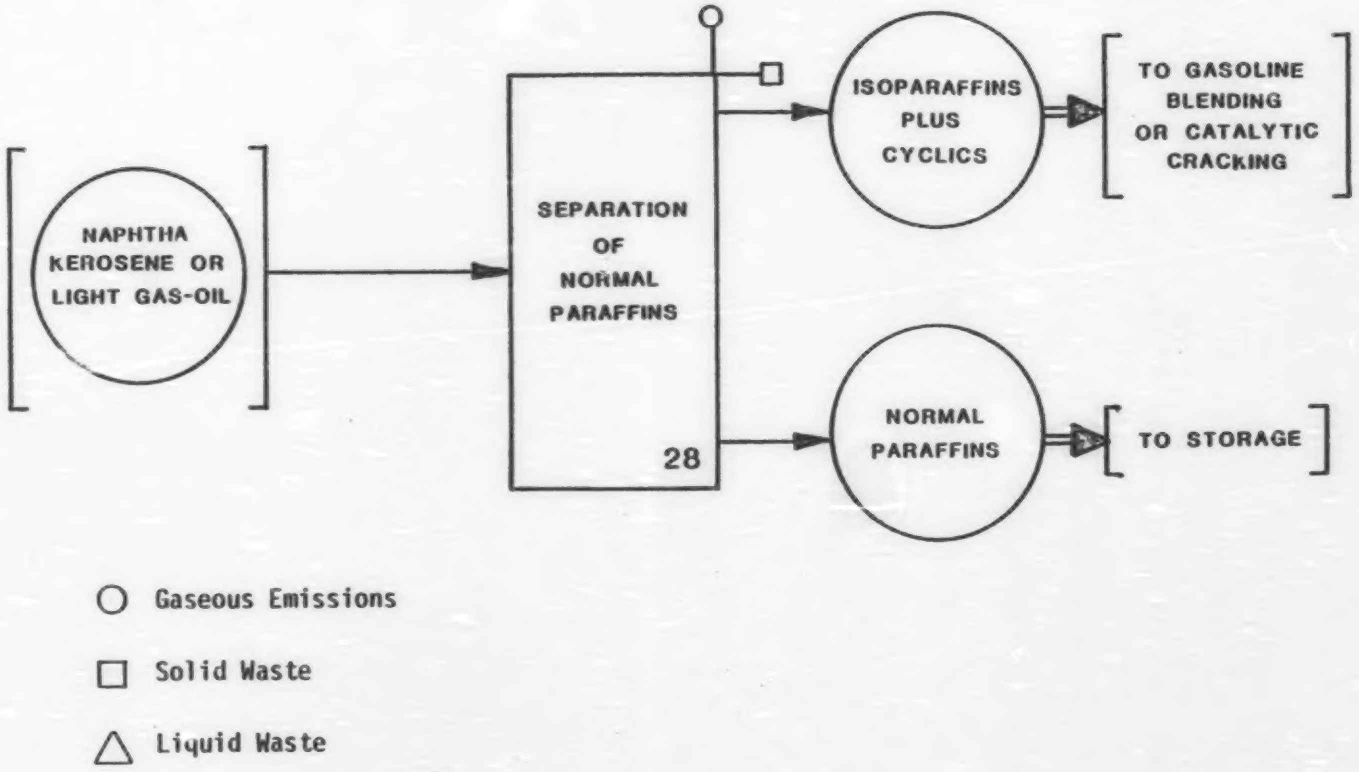

NAPHTHA
KEROSENE OR
LIGHT GAS-OIL
SEPARATION
OF
NORMAL
PARAFFINS
28
ISOPARAFFINS
PLUS
CYCLICS
TO GASOLINE
BLENDING
OR CATALYTIC
CRACKING
NORMAL
PARAFFINS
TO STORAGE
○ Gaseous Emissions
□ Solid Waste
△ Liquid Waste

Figure 10. NORMAL PARAFFIN PRODUCTION PROCESSES

Separation of Normal Paraffins

1. Function - In this process normal paraffins as a class are separated from branched and cyclic hydrocarbons. The feed may be a naphtha, kerosene or light gas-oil. The two product streams consist of normal paraffins in one stream and a raffinate essentially free (less than 1%) from normal paraffins in the other stream. The raffinate from light naphthas is used as a component of gasoline. The raffinate from kerosene feed is suitable only as a catalytic cracker feedstock.

The separation is effected by adsorption of the normal paraffin portion of the feed onto synthetic zeolites (molecular sieves). The adsorption phase of the process may be carried out with the feed in the vapor phase or the liquid phase depending on the exact process. Branched and cyclic compounds are not adsorbed and become the raffinate. The normal paraffin product is removed from the artificial zeolite by a reduction in pressure, by elution with a recycle stream of light normal paraffins, or by heating. Adsorption-desorption may be carried out in a series of vessels cyclically or in a single vessel continuously. Separation of product from the elution stream may be effected by distillation.

The uses of the product depend on the nature of the feed. A light naphtha yields normal paraffins in the C_5-C_7 range for use as hydrocarbon specialty solvents. A kerosene feed yields normal paraffins in the C_{10}-C_{13} or C_{10}-C_{15} range depending on the breadth of the cut of the feedstock.

2. Input Materials - Naphthas, kerosenes, and light gas-oils are used as feedstocks. The boiling fraction used will depend on the product desired. The yield of normal paraffins depends on the normal paraffin content of the feed. The separation is quite effective. The normal paraffin product typically contains no more than 1 to 2% branched and cyclic compounds and the raffinate typically contains no more than 1 to 2% normal compounds. Feeds containing 20 to 40% normal paraffins are typical. Coking consumes a small fraction of the feedstock, especially in those processes which use adsorption from the vapor phase.

3. Operating Parameters - The capacity of units reported to be in operation in 1971 ranged from 27 to 110 Gg/year (60-240×10^6 lbs/yr). Precise operating conditions were not available but were reported to be within the temperature and pressure ranges common to refinery and petrochemical operations.

4. Utilities - Utility requirements vary according to process and feedstock. Typical requirements for the Iso Siv (Union Carbide Corporation,

Linde Division) process for naphtha feeds and for kerosene feeds are listed in Table 50 below.

Table 50. UTILITY REQUIREMENTS FOR ISO SIV PROCESS

		Naphtha Feed	Kerosene Feed
Process Heat	MJ/kg n-paraffin product	1.3	6.9
	Btu/lb n-paraffin product	560	2,960
Electric Power	kWh/kg n-paraffin product	0.066	0.053
	kWh/kg n-paraffin product	0.030	0.024
Cooling Water	m^3/kg n-paraffin product	0.0267	0.0876
	gallons/lb n-paraffin product	3.2	10.5

Source: "Petrochemical Handbook." Hydrocarbon Processing, 54 (November 1975), 167.

"Refining Handbook." Hydrocarbon Processing, 49 (September 1970), 271, 273.

"Refining Handbook." Hydrocarbon Processing, 53 (September 1974), 199, 203.

5. Waste Streams - This is primarily a separation process and there are no waste streams as such. Coking occurs in the vapor-phase adsorption processes, and the de-coking operation can be expected to release particulates, sulfur oxides and carbon monoxide to the atmosphere. Fugitive emissions of light hydrocarbons can be expected from pump seals, valves and relief vents. Atmospheric emissions from process heaters are described in Process 31 for the Petroleum Refining Industry. Waste streams resulting from cooling water treatment are discussed in the Industry Description. Costs for chemicals are listed in economic descriptions of this process, but the process description gives no information as to the type of chemicals used or their fate. Spent sorbent represents a solid waste which is landfilled.

6. EPA Source Classification Code - None exists.

7. References -

(1) Considine, Douglas M., ed. Chemical and Process Technology Encylcopedia. N.Y.: McGraw-Hill Book Company, 1974.

(2) Hahn, Albert V. The Petrochemical Industry, Market and Economics. N.Y.: McGraw-Hill Book Company, 1970.

(3) Hedley, W. H., et al. Potential Pollutants from Petrochemicals Processes. MRC-DA-406. Dayton, Ohio: Monsanto Research Corp., December 1973.

(4) "Petrochemical Handbook." Hydrocarbon Processing, 50 (November 1971), 184.

(5) "Petrochemical Handbook." Hydrocarbon Processing, 52 (November 1973), 154.

(6) "Petrochemical Handbook." Hydrocarbon Processing, 54 (November 1975), 167.

(7) "Refining Handbook." Hydrocarbon Processing, 49 (September 1970), 271, 273.

(8) "Refining Handbook." Hydrocarbon Processing, 53 (September 1974), 199, 203.

APPENDIX A

RAW MATERIALS

Preceding page blank

Table A-1 HYDROCARBON RAW MATERIALS FOR THE BASIC PETROCHEMICALS INDUSTRY

Raw Material	Description
Naphtha	petroleum fraction boiling in the approximate range of 90 to 200°C (200-400°F).
Kerosene	petroleum fraction with boiling range of 180 to 300°C (360-570°F)
Gas Oil	petroleum distillate with boiling range of 230 to 430°C (450-800°F)
Natural Gas Liquids	ethane, ethane/propane, propane, butane and higher products from Oil and Gas Production Industry
Refinery Gases	gases from cracking, light ends from crude distillation, etc. Composition variable
Butylenes	C_4 olefins from refinery gases
Heavy Feedstocks	crude oil or residuals (see The Petroleum Refining Industry for composition)
Caustic Extract	from refinery treatment of distillates. Contains tar acids and thiols
Catalytic Reformate	C_6-C_9 fraction and heavier fraction from catalytic reforming of naphthas. Highly cyclic-naphthenic and aromatic
Pyrolysis Gasoline	from olefins production
Mixed C_4 Stream	from olefins production
Catalytic Cycle Oil	heavy oils from bottom of distillation column following catalytic cracking. Boiling range about 200 to 290°C (400-550°F).
Thermal Cracking Bottoms	sludge from olefins plant

APPENDIX B
PRODUCTS

Table B-1 PRODUCTS AND BY-PRODUCTS OF THE BASIC PETROCHEMICALS INDUSTRY

Operation	Products	By-products
Olefins Production	ethylene propylene	pyrolysis gasoline mixed C_4 stream hydrogen methane fuel oil
Butadiene Production	normal butenes butadiene isobutylene or polymerized product	
BTX Production	benzene toluene mixed or solvent xylenes ethylbenzene ortho-xylene para-xylene meta-xylene	C_9 aromatics fuel gas (methane) raffinate containing paraffins and naphthenes suitable for cracking feedstock
Naphthalene Production	naphthalene	fuel gas high octane naptha or benzene heavy oil rich in aromatics
Production of Cresols and Cresylic Acids	meta-, para-cresol mixture ortho-cresol xylenols phenol cresylic acids	thiocresylic acids and derivatives of thiophenol
Separation of Normal Paraffins	C_5-C_7 normal paraffins	gasoline blending stock containing branched chain and cyclic compounds
	C_{10}-C_{13} or C_{10}-C_{15} normal paraffins	catalytic cracking feedstock containing branched chain and cyclic compounds

APPENDIX C

PRODUCERS OF BASIC PETROCHEMICALS AND PRODUCTION LOCATIONS

Table C-1. BENZENE PRODUCERS

Company	Location	1975 Capacity Gg (10^6 lb)[a]	Uses
Allied Chemical Corporation	Winnie, Texas	10 (20)	Styrene; phenol; synthetic detergents; cyclohexane for nylon; aniline; DDT; maleic anhydride; dichlorobenzene; benzene hexachloride; nitrobenzene; diphenyl; insecticides, fumigants; solvent; paint remover; rubber cement; antiknock gasoline.
Amerada Hess Corporation	St. Croix, Virgin Islands	50 (110)	
American Petrofina, Inc.	Port Arthur, Texas	50 (110)	
Ashland Oil, Inc.	Ashland (Catlettsburg), Kentucky	166 (365)	
	Tonawanda (Buffalo), New York	50 (110)	
Atlantic Richfield Company	Houston, Texas	148 (325)	
	Wilmington, Delaware	54 (120)	
	Bethlehem, Pennsylvania	9 (20)	
	Lackawanna, New York	25 (55)	
	Sparrows Point, Maryland	50 (110)	
Atlantic Richfield Co./Union Oil Company of Calif.	Nederland, Texas	68 (150)	
Charter International Oil Co.	Houston, Texas	16 (35)	
Cities Service Co., Inc.	Lake Charles, Louisiana	84 (185)	
Coastal States Gas Producing Co.	Corpus Christi, Texas	234 (515)	

Table C-1. (Cont'd) BENZENE PRODUCERS

Company	Location	1975 Capacity Gg (10^6 lb)[d]	Uses
Commonwealth Oil Refining Company	Penuelas, Puerto Rico	617 (1360)	
Cosden Oil & Chemicals	Big Spring, Texas	100 (220)	
Crown Central Petroleum Corp.	Pasadena, Texas	66 (145)	
The Dow Chemical Company	Bay City, Michigan	100 (220)	
	Freeport, Texas	134 (295)	
Exxon Corp.	Baton Rouge, Louisiana	241 (530)	
	Baytown, Texas	207 (455)	
Gulf Oil Corp.	Alliance, Louisiana	234 (515)	
	Philadelphia, Pennsylvania	109 (240)	
	Port Arthur, Texas	127 (280)	
	Toledo, Ohio	2 (5)	
Kerr-McGee Corp.	Corpus Christi, Texas	27 (60)	
Marathon Oil Co.	Detroit, Michigan	23 (50)	
	Texas City, Texas	20 (45)	
Mobil Oil Corp.	Beaumont, Texas	200 (440)	
Monsanto Company	Alvin (Chocolate Bayou), Texas	250 (550)	
Penzoil United, Inc.	Shreveport, Louisiana	41 (90)	
Phillips Petroleum Company	Sweeny, Texas	73 (160)	
	Guayama, Puerto Rico	367 (810)	

Table C-1. (Cont'd) BENZENE PRODUCERS

Company	Location	1975 Capacity Gg (10^6 lb)[a]	Uses
Shell Oil Company	Deer Park, Texas	250 (550)	
	Odessa, Texas	16 (35)	
	Wilmington, Calif.	66 (145)	
	Wood River, Illinois	134 (295)	
Skelly Oil Company	El Dorado, Kansas	48 (105)	
Southwestern Oil & Refining Co.	Corpus Christi Texas	30 (65)	
Standard Oil Company of California	El Segundo, California	50 (110)	
Standard Oil Company of Indiana	Texas City, Texas	284 (625)	
Standard Oil Company (New Jersey)	Baton Rouge, Louisiana	222 (490)	
	Baytown, Texas	222 (490)	
Standard Oil Company (Ohio)	Port Arthur, Texas	57 (125)	
Sun Oil Company	Marcus Hook, Pennsylvania	50 (110)	
	Corpus Christi, Texas	100 (220)	
	Tulsa, Oklahoma	79 (175)	
Tenneco, Inc.	Chalmette, Louisian	34 (75)	
Texaco, Inc.	Port Arthur, Texas	150 (330)	
	Westville. New Jersey	116 (255)	
Union Carbide Corporation	Taft, Louisiana	166 (365)	

Table C-1. (Cont'd) BENZENE PRODUCERS

Company	Location	1975 Capacity Gg (10^6 lb)[a]	Uses
Union Oil Company of California	Lemont, Illinois	109 (240)	
Union Pacific Corporation	Corpus Christi, Texas	34 (75)	
	Total capacity 1975	6.11 Tg/yr (13,670 x 10^6 lb/yr)	

---

[a] Estimates assumed accurate to the nearest 5 x 10^6 lb. Conversions made to the same number of significant figures or to the nearest Gg.

[b] This compares favorably with total production reported in Chemical and Engineering News for benzene in 1973 (5.42 Tg, 1190 x 10^6 lb) and in 1974 (5.65 Tg, 1240 x 10^6 lb). Of the 1974 total, 0.672 Tg (1480 x 10^6 lb) was produced from coke batteries, coke oven materials shipped to petroleum refineries and coal tar distillation plants.

Source: Monsanto Research Corporation

Table C-2. BUTADIENE PRODUCERS

Company	Location	Capacity Gg (10^6lb)/yr[a]	Uses
Arco Chemical Company	Channelview, Texas	127 (280)	Styrene-butadiene rubber, polybutadiene and nitrile elastomers; adiponitrile (Nylon 66); latex paints; resins; organic intermediates; ABS plastics.
Copolymer Rubber & Chemical Corp.	Baton Rouge, Louisiana	58 (130)	
Dow Chemical U.S.A.	Bay City, Michigan	11 (25)	
	Freeport, Texas	39 (85)	
El Paso Natural Gas Co.	Odessa, Texas	91 (200)	
Exxon Corp.	Baton Rouge, Louisiana	154 (340)	
The Firestone Tire and Rubber Co.	Orange, Texas	100 (220)	
Getty Oil Co.	Delaware City, Delaware	9 (20)	
Mobile Oil Corp.	Beaumont, Texas	36 (80)	
Monsanto Co.	Chocolate Bayou, Texas	55 (120)	
Neches Butane Products Co.	Port Neches, Texas	290 (640)	
Northern Natural Gas	Morris, Illinois	30 (65)	
Petro-Tex Chemical Corp.	Houston, Texas	450 (990)	
Phillips Petroleum Co.	Phillips, Texas	130 (290)	
Puerto Rico Olefins Co.	Penuelas, Puerto Rico	90 (200)	
Shell Chemical Co.	Deer Park, Texas	120 (265)	
Standard Oil (Indiana)	Chocolate Bayou, Texas	41 (90)	

Table C-2. (Continued) BUTADIENE PRODUCERS

Company	Location	Capacity Gg (10 lb)/hr[a]	Uses
Union Carbide Corp.	Seadrift, Texas	20 (45)	
	Taft, Louisiana	41 (90)	
	Texas City, Texas	20 (45)	
	Penuelas, Puerto Rico	70 (155)	
Total		1985 (4375)	

---

[a] Estimates assumed accurate to the nearest 5 x 10^6 lbs. Conversions made to the same number of significant figures or to the nearest Gg.

Source: Monsanto Research Corporation

Table C-3. CRESOLS AND CRESYLIC ACIDS PRODUCERS[a]

Company	Location	Capacity[b] Gg (10^6lb)/yr	Uses
Merichem Co.	Houston, Texas	45 (100)	Phosphate esters, magnet wire, antioxidants, resins, cleaning and disinfectant, ore flotation.
Northwest Petroleum	Anacortes, Washington	7 (15)	
Pitt-Consol	Newark, New Jersey	23 (50)	
Products Chem. Co.	Santa Fe Springs, California	14 (30)	
Total		89 (195)	

---

[a] Recovery from petroleum sources. Some synthetic production reported at Pitt-Consol.

[b] Estimates assumed accurate to the nearest 5 x 10^6 lbs. Conversions made to the same number of significant figures or to the nearest Gg.

Source: Hedley, W.H., et al. Potential Pollutants From Petrochemical Processes. MRC-DA-406. Dayton, Ohio: Monsanto Research Corp., Decmeber 1973.

Table C-4. ETHYLENE PRODUCERS

Company	Location	Capacity as of[a] 31 December 1974 Gg (10^6 lb)/yr	Uses
Allied Chemical Corp., BASF Wyandotte Corp., Borg-Warner Corp.	Geismar, Louisiana	340 (750)	Manufacture of ethyl alcohol, ethylene glycols, ethylene dichloride, aluminum alkyls, vinyl chloride, ethyl chloride, ethylene oxide, ethylene chlorohydrin, acetaldehyde, linear alcohols, polystyrene, styrene, polyethylene, polyvinyl chloride, SBR, polyester resins, trichloroethylene, etc.; refrigerant; cryogenic research; agricultural chemistry; welding and cutting of metals, anesthetic.
Arco Chemical Company	Wilmington, California	45 (100)	
Arco/Polymers, Inc.	Houston, Texas	227 (500)	
Chemplex Company	Clinton, Iowa	277 (500)	
Cities Service Company, Inc.	Lake Charles, Louisiana	426 (940)	
Conoco Chemicals	Lake Charles, Louisiana	295 (650)	
Dow Chemical U.S.A.	Bay City/Midland, Michigan	77 (170)	
	Freeport/Oyster Creek, Texas	1.1 Tg (2500)	
	Plaquemine, Louisiana	499 (1100)	
E.I. du Pont de Nemours & Co., Inc.	Orange, Texas	340 (750)	
Eastman Chemical Products, Inc.	Longview, Texas	363 (800)	
El Paso Products Co., Dart Industries, Inc.	Odessa, Texas	234 (517)	
Exxon Chemical Company, U.S.A.	Baton Rouge, Louisiana	771 (1700)	
	Baytown, Texas	32 (70)	
B.F. Goodrich Chemical Company	Calvert City, Kentucky	159 (350)	

Table C-4. (Continued) ETHYLENE PRODUCERS

Company	Location	Capacity as of[a] 31 December 1974 Gg (10^6 lb)/yr	Uses
Gulf Oil Chemicals Company	Cedar Bayou, Texas	190 (420)	
	Port Arthur, Texas	522 (1150)	
Jefferson Chemical Company, Inc.	Port Neches, Texas	239 (525)	
Mobil Chemical Company	Beaumont, Texas	213 (470)	
Monsanto Company	Alvin (Chocolate Bayou), Texas City, Texas	363 (800)	
National Distillers & Chemical Corp.	Tuscola, Illinois	159 (350)	
Northern Petrochemical Company	East Morris (Joliet), Illinois	363 (800)	
Olin Corporation	Brandenburg, Kentucky	54 (120)	
Petro Gas Producing Co.	Port Arthur, Texas	9 (20)	
Phillips Petroleum Company	Sweeney, Texas	517 (1140)	
Puerto Rico Olefins Company	Penuelas, Puerto Rico	454 (1000)	
Shell Oil Company	Deer Park, Texas	680 (1500)	
	Norco, Louisiana	249 (550)	
Sunolin Chemical Company	Claymont, Delaware	102 (225)	
Union Carbide Corporation	Seadrift, Texas	549 (1210)	
	Taft, Louisiana	186 (410)	

Table C-4. (Continued) ETHYLENE PRODUCERS

Company	Location	Capacity as of[a] 31 December 1974 Gg (10^6 lb)/yr	Uses
Union Carbide Corporation (Continued)	Texas City, Texas	77 (170)	
	Torrance, California	77 (170)	
	Whiting, Indiana	68 (150)	
Union Carbide Caribe, Inc.	Penuelas, Puerto Rico	351 (775)	
Total		11.242 Tg (24,780)[b]	

---

[a] Estimates assumed accurate to the nearest 5 x 10^6 lbs. Conversions made to the same number of significant figures or to the nearest Gg.

[b] This is comparable to production figures reported by Chemical and Engineering News for 1973 (10.128 Tg (22,329 x 10^6 lb)) and 1974 (10.669 Tg (23,522 x 10^6 lb)).

Source: Monsanto Research Company

Table C-5. NAPHTHALENE PRODUCERS[a]

Company	Location	Capacity Gg (10^6 lb)/yr[b]	Uses
Ashland Oil, Inc.	Ashland, Kentucky	45 (100)	Phthalic anhydride manufacture; insecticides; dyestuffs; synthetic tanning agents.
Getty Oil Co.	Delaware City. Delaware	45 (100)	
Kewanee Oil Co.	Solon, Ohio	Not Available	
Monsanto Co.	Chocolate Bayou, Texas	45 (100)	
Sun Oil Co.	Toledo, Ohio	68 (150)	

---

[a] From Petroleum Sources

[b] Estimates assumed accurate to the nearest 5 x 10^6 lbs. Conversions made to the same number of significant figures or to the nearest Gg.

Source: Stanford Research Institute. 1975 Directory of Chemical Producers, U.S.A. Menlo Park, California: 1975.

Table C-6. MIXED XYLENES PRODUCERS[a]

Company	Location	Capacity as of 1 July 1971 Gg (10^6 lb)/yr[b]	Uses
American Petrofina, Inc.	Big Springs, Texas	59 (130)	Aviation gasoline; protective coatings; solvent for alkyd resins, lacquers, enamels, rubber cements; synthesis of organic chemicals.
Ashland Oil, Inc.	Ashland, Kentucky	81 (180)	
	Buffalo (Tonawanda), New York	50 (110)	
Atlantic Richfield Company	Houston, Texas	196 (430)	
Atlantic Richfield Co., Union Oil Company of California	Nederland, Texas	81 (180)	
Charter International Oil Co.	Houston, Texas	72 (160)	
Cities Service Company, Inc.	Lake Charles, Louisiana	236 (520)	
Coastal States Gas Producing Co.	Corpus Christi, Texas	77 (170)	
Commonwealth Oil Refining Co., Inc.	Penuelas, Puerto Rico	259 (570)	
Crown Central Petroleum Co.	Houston, Texas	45 (100)	
Marathon Oil Company	Detroit, Michigan	16 (35)	
	Texas City, Texas	45 (100)	
Monsanto Company	Alvin (Chocolate Bayou), Texas	134 (295)	
Phillips Petroleum Company	Guayama, Puerto Rico	327 (720)	
Shell Oil Company	Deer Park (Houston), Texas	229 (505)	
Southwestern Oil & Refining Co.	Corpus Christi, Texas	59 (130)	

Table C-6. (Continued) MIXED XYLENES PRODUCERS[a]

Company	Location	Capacity as of 1 July 1971 Gg (10^6 lb)/yr[b]	Uses
Standard Oil of California	El Segundo, California	75 (165)	
	Pascagoula, Mississippi	211 (465)	
	Richmond, California	159 (350)	
Standard Oil Co. (Indiana)	Texas City, Texas	488 (1075)	
Standard Oil Co. (New Jersey)	Baytown, Texas	390 (860)	
Sun Oil Company	Marcus Hook, Pennsylvania	98 (215)	
	Corpus Christi, Texas	114 (250)	
Tenneco, Inc.	Chalmette, Louisiana	163 (360)	
Union Carbide Corp.	Taft, Louisiana	32 (70)	
Union Oil Co. of California	Lemont, Illinois	32 (70)	
Union Pacific Railroad Co.	Corpus Christi, Texas	59 (130)	
Total		3.79 Tg (8340)[c]	

---

[a] Production from petroleum.

[b] Estimates assumed accurate to the nearest 5 x 10^6 lbs. Conversions made to the same number of significant figures or to the nearest Gg.

[c] According to Chemical and Engineering News, production for 1973 (2.56 Tg [5635 x 10^6 lb]) and 1974 (5770 x 10^6 lb [2.62 Tg]) was down somewhat from 1970-1971.

Source: Monsanto Research Corporation

Table C-7. NORMAL PARAFFINS PRODUCERS[a]

Company	Location	Capacity Gg (10^6 lb)/yr[b]	Uses
Continental Oil Co.	Baltimore, Maryland	Not Available	C_5- C_7 used for speciality solvents; C_{10}- C_{13} used for manufacture of biodegradable detergents, plasticizers, alcohols, fatty acids, proteins, fire retardants.
	Westlake, Louisiana	102 (225)	
Exxon Corp.	Baytown, Texas	100 (220)	
Shell Chem. Co.	Deer Park, Texas	45 (100)	
South Hampton Co.	Silsbee, Texas	27 (60)	
Union Carbide Corp.	Texas City, Texas	109 (240)	

---

[a] C_{10}- C_{15} range capacity data.

[b] Estimates assumed accurate to the nearest 5 x 10^6 lb. Conversions made to the same number of significant figures or to the nearest Gg.

Source: Chemical Marketing Reporter, 18 February 1974.

Hedley, W.H., et al. Potential Pollutants From Petrochemical Processes. MRC-DA-406. Dayton, Ohio: Monsanto Research Corp., December 1973.

Table C-8. PROPYLENE PRODUCERS

Company	Location	Capacity as of[a] 1 May 1975 Gg (10^6 lb)/yr	Uses
Allied Chemical Corp., BASF Wyandotte Corp., Borg-Warner Chemicals	Geismar, Louisiana	23 (50) (chemical grade)	Isopropyl alcohol, polypropylene, synthetic glycerol, acrylonitrile, propylene oxide, heptene, cumene, polymer gasoline, anticipated use in acrylic acid and in vinyl resins
Amerada Hess Corporation	Port Reading, New Jersey	59 (130) (polymer grade)	
Amoco Chemicals Corp.	Alvin (Chocolate Bayou), Texas	179 (395) (chemical grade)	
	Texas City, Texas	166 (365) (chemical & polymer grade)	
	Whiting, Indiana	91 (200)	
	Wood River, Illinois	59 (130)	
Ashland Oil, Inc.	Ashland (Catlettsburg), Kentucky	75 (165)	
	Louisville, Kentucky	14 (30)	
	Tonawanda, New York	23 (50)	
Atlantic Richfield Co.	Channelview, Texas	98 (215) (chemical & refinery grade)	
	Wilmington, California	77 (170) (chemical grade)	
	Houston, Texas	54 (120) (chemical grade)	
Charter International Oil Co.	Houston, Texas	34 (75) (chemical grade)	
Chemplex Co.	Clinton, Iowa	59 (130) (chemical grade)	
Chevron Chemical Co.	El Segundo, California	95 (210) (chemical grade)	
	Lake Charles, Louisiana		

Table C-8. (Continued) PROPYLENE PRODUCERS

Company	Location	Capacity as of[a] 1 May 1975 Gg (10^6 lb)/yr	Uses
Chevron Chemical Company	Lake Charles, Louisiana	240 (530) (polymer grade)	
Clark Oil & Refining Corporation	Blue Island, Illinois	32 (70)	
Cosden Oil & Chemical Company	Big Spring, Texas	59 (130)	
	El Dorado, Kansas	16 (35)	
	Mt. Pleasant	25 (55)	
Dart Industries, Inc., Rexene Polymers Co./El Paso Products Co.	Odessa, Texas	79 (175) (polymer grade)	
Dow Chemical U.S.A.	Bay City/Midland, Michigan	45 (100) (chemical grade)	
	Freeport, Texas	272 (600) (chemical grade)	
	Plaquemine, Louisiana	95 (210) (chemical grade)	
E.I. du Pont de Nemours & Co.	Orange, Texas	61 (135) (chemical grade)	
Exxon Chemical Company, U.S.A.	Baton Rouge, Louisiana	508 (1,120) (chemical grade)	
	Baytown, Texas	249 (550) (polymer grade)	
	Bayway, New Jersey	145 (320) (polymer grade)	
B.F. Goodrich Chemical Co.	Calvert City, Kentucky	64 (140) (chemical grade)	

Table C-8. (Continued) PROPYLENE PRODUCERS

Company	Location	Capacity as of[a] 1 May 1975 Gg (10^6 lb)/yr	Uses
Gulf Oil Corp.	Cedar Bayou, Texas	57 (125) (polymer grade)	
	Port Arthur, Texas	168 (370) (polymer grade)	
Jefferson Chemical Company, Inc.	Port Neches, Texas	59 (130) (chemical grade)	
Marathon Oil Co.	Detroit, Michigan	45 (100) (chemical grade)	
	Texas City, Texas	91 (200) (chemical grade)	
Mobile Oil Corp.	Beaumont, Texas	109 (240) (chemical & polymer grade)	
Monsanto Company	Alvin (Chocolate Bayou) Texas City, Texas	249 (550) (chemical grade)	
Northern Petrochemical Co.	Joliet (near East Morris), Illinois	91 (200) (polymer grade)	
Petro Gas Producing Co.	Port Arthur, Texas	29 (65) (chemical grade)	
Phillips Petroleum Company	Sweeney, Texas	59 (130) (polymer grade)	
Puerto Rico Olefins Company	Penuelas, Puerto Rico	295 (650) (polymer grade)	
Shell Oil Company	Deer Park, Texas	431 (950) (chemical grade)	
	Norco, Louisiana	100 (220) (chemical & polymer grade)	
Sun Oil Company	Corpus Christi, Texas	50 (110) (chemical grade)	

Table C-8. (Continued) PROPYLENE PRODUCERS

Company	Location	Capacity as of[a] 1 May 1975 Gg (10^6 lb)/yr	Uses
Sun Oil Company	Marcus Hook, Pennsylvania	154 (340) (polymer grade)	
Texas City Refining, Inc.	Texas City, Texas	45 (100) (chemical grade)	
Texas Eastman Company	Longview, Texas	>181 (>400) (chemical & polymer grade)	
Union Carbide Corp.	Seadrift, Texas	50 (110) (chemical grade)	
	Taft, Louisiana	91 (200) (chemical grade)	
	Texas City, Texas	109 (240) (chemical grade)	
	Whiting, Indiana	125 (275) (chemical grade)	
	Ponce (Penuelas) Puerto Rico	209 (460) (chemical grade)	
Vistron Corporation	Lima, Ohio	122 (270) (chemical grade)	
Total		5.915 Tg (13,040)	

---

[a] Estimates assumed accurate to the nearest 5 x 10^6 lb. Conversions made to the same number of significant figures or to the nearest Gg.

Source: Monsanto Research Corporation

Table C-9. TOLUENE PRODUCERS[a]

Company	Location	Capacity as of 1 September 1972 Gg (10^6 lb)/yr[b]	Uses
Amerada Hess Corporation	St. Croix, Virgin Islands	130 (290)	
American Petrofina, Inc.	Big Spring, Texas	50 (110)	
Ashland Oil, Inc.	Ashland (Catlettsburg), Kentucky	98 (215)	
	Tonawanda (Buffalo), New York	66 (145)	
Atlantic Richfield Company	Houston, Texas	118 (260)	
	Wilmington, California	73 (160)	
Charter International Company	Houston, Texas	52 (115)	
Coastal States Gas Producing Co.	Corpus Christi, Texas	98 (215)	
Commonwealth Oil Refining Co., Inc.	Penuelas, Puerto Rico	66 (145)	
Crown Central Petroleum Corp.	Houston, Texas	46 (100)	
The Dow Chemical Company	Bay City, Michigan	59 (130)	
Gulf Oil Corp.	Philadelphia, Pennsylvania	66 (145)	
	Port Arthur, Texas	27 (60)	
Marathon Oil Co.	Detroit, Michigan	50 (110)	
	Texas City, Texas	43 (95)	
Mobil Oil Corp.	Beaumont, Texas	229 (505)	

Table C-9. (Continued) TOLUENE PRODUCERS[a]

Company	Location	Capacity as of 1 September 1972 Gg (10^6 lb)/yr[b]	Uses
Monsanto Company	Alvin (Chocolate Bayou), Texas	147 (325)	
Phillips Petroleum Company	Sweeney, Texas	32 (70)	
	Guayama, Puerto Rico	263 (580)	
Shell Oil Company	Deer Park, Texas	163 (360)	
Southwestern Oil & Refining Co.	Corpus Christi, Texas	66 (145)	
Standard Oil Co. of California	El Segundo, California	66 (145)	
Standard Oil Co. (Indiana)	Texas City, Texas	524 (1155)	
Standard Oil Co. (New Jersey)	Baton Rouge, Louisiana	213 (470)	
	Baytown, Texas	213 (470)	
The Standard Oil Company (Ohio)	Marcus Hook, Pennsylvania	27 (60)	
	Port Arthur, Texas	59 (130)	
Sun Oil Company	Marcus Hook, Pennsylvania	100 (220)	
	Tulsa, Oklahoma	66 (145)	
	Corpus Christi, Texas	79 (175)	
Swift and Company	Potwin, Kansas	39 (85)	
Tenneco, Inc.	Chalmette, Louisiana	50 (110)	
Texaco, Inc.	Westville, New Jersey	98 (215)	

Table C-9. (Continued) TOLUENE PRODUCERS[a]

Company	Location	Capacity as of 1 September 1972 Gg (10^6 lb)/yr[b]	Uses
Union Carbide Corporation	Taft, Louisiana	66 (145)	
Union Oil of California	Lemont, Illinois	59 (130)	
	Beaumont, Texas	66 (145)	
Union Pacific Corporation	Corpus Christi, Texas	43 (95)	
Total		3.71 Tg (8175)[c]	

---

[a] Petroleum producers only

[b] Estimates assumed accurate to the nearest 5 x 10^6 lb. Conversions made to the same number of significant figures or to the nearest Gg.

[c] Chemical and Engineering News production figures for 1973 were 3.13 Tg (6915 x 10^6 lb), and in 1974 were 3.40 Tg (7495 x 10^6 lb).

Source: Monsanto Research Corporation

Table C-10. BASIC PETROCHEMICAL PRODUCTION SITES DIRECTLY ASSOCIATED WITH PETROLEUM REFINERIES (CLASSES 2, 3, and 4A)[1,2]

Classification[2]	Company	Site	Product[3]
2	Allied Chemical Corp.	Winnie, TX	B, NP
3	Amerada Hess Corp.	Port Reading, NJ	P
2	Amerada Hess Corp.	St. Croix, VI	B, T, X
4A	American Petrofina, Inc.	Port Arthur, TX	B, T
4A	Arco Chemical Co.	East Chicago, IN	P
4A	Arco Chemical Co.	Houston, TX	B, EB, E, P, T, X, OX, PX
4A	Ashland Chemical Co.	Ashland, KY	B, N, P, T, X
3	Ashland Chemical Co.	Louisville, KY	P
2	Ashland Chemical Co.	North Tonawanda, NY	B, P, T, X
4A	Charter Chemicals	Houston, TX	B, EB, P, T, X, PX
4A	Chevron Chemical Co.	El Segundo, CA	B, P, T, PX
2	Chevron Chemical Co.	Pascogoula, MS	T, PX
4A	Chevron Chemical Co.	Richmond, CA	BT, P, OX, PX, NP
3	Cities Service Co., Inc.	Lake Charles, LA	B, E, P, X, OX, PX
4A	Clark Chemical Co.	Blue Island, IL	P
4A	Coastal States Gas Co.	Corpus Christi, TX	B, P, T, X, OX
4A	Commonwealth Oil Refining Co.	Penuelas, PR	B, EB, T, X, OX
4A	Continental Oil Co.	Westlake, LA	OC, C, CA, E, P, NP
4A	Cosden Oil and Chemical Co.	Big Spring, TX	B, EB, BT, P, T, X, OX
3	Cosden Oil and Chemical Co.	El Dorado, KA	P
3	Cosden Oil and Chemical Co.	Mt. Pleasant, TX	P
2	Crown Central Petroleum Corp.	Pasadena, TX	B, T, X, OX
4A	El Paso Natural Gas Co.	Odessa, TX	BT, EB, E, P
4A	Exxon Chemical Co.	Baton Rouge, LA	B, BT, E, P
4A	Exxon Chemical Co.	Baytown, TX	B, E, BT, P, OX, PX, NP
4A	Exxon Chemical Co	Baytown, NJ	BT, P, T
4A	Getty Oil Co.	Delaware City, DE	BT, N, P
2	Gulf Oil Co.	Alliance, LA	B, X
4A	Gulf Oil Co.	Philadelphia, PA	B, P, T
4A	Gulf Oil Co.	Port Arthur, TX	B, E, P, T
2	Hercor Chemical Corp	Penuelas, PR	PX

Table C-10. (Continued) BASIC PETROCHEMICAL PRODUCTION SITES DIRECTLY ASSOCIATED WITH PETROLEUM REFINERIES (CLASSES 2, 3, and 4A)[1,2]

Classification[2]	Company	Site	Product[3]
3	Marathon Oil Co.	Detroit, MI	P
4A	Marathon Oil Co.	Robinson, IL	AN
4A	Marathon Oil Co.	Texas City, TX	B, P, T, X
4A	Mobil Oil Corp.	Beaumont, TX	B, BT, CA, E, P, T
3	Mobil Oil Corp.	Paulsboro, NJ	CA
4A	Northern Natural Gas Corp.	Morris, IL	BT, E, P
3	Oil Shale Corp.	El Dorado, AR	P
2	Penzoil Co.	Shreveport, LA	B, NP
2	Phillips Petroleum Co.	Borger, TX	P
4A	Phillips Petroleum Co.	Guayama, PR	B, T, X, OX, PX
4A	Phillips Petroleum Co.	Sweeny, TX	B, E, P, T
4A	Puerto Rico Olefins Co.	Penuelas, PR	BT, E, P
4A	Shell Oil Co.	Deer Park, TX	B, BT, E, P, T, X, OX, PX NP
4A	Shell Oil Co.	Norco, LA	E, P
2	Shell Oil Co.	Odessa, TX	B
2	Shell Oil Co.	Wilmington, CA	B
4A	Shell Oil Co.	Wood River, IL	B
4A	Skelly Oil Co.	El Dorado, KA	B, P, T
2	South Hampton Co.	Silsbee, TX	NP, X
4A	Standard of Indiana	Chocolate Bayou, TX	BT, E, P
4A	Standard of Indiana	Decature, AL	PX
4A	Standard of Indiana	Texas City, TX	B, EB, BT, P, T, X, PX
4A	Standard of Indiana	Wood River, IL	BT, P
4A	Standard of Indiana	Yorktown, VA	H
4A	Standard of Ohio	Lima, OH	P
2	Standard of Ohio	Marcus Hook, PA	T
3	Standard of Ohio	Toledo, OH	P
4A	Sunoco	Corpus, Christi, TX	B, EB, P, T, X, OX, PX
4A	Sunoco	Duncan, OK	P
4A	Sunoco	Marcus Hook, PA	B, P, T, X
4A	Sunoco	Toledo, OH	N, P

Table C-10.(Continued) BASIC PETROCHEMICAL PRODUCTION SITES DIRECTLY ASSOCIATED WITH PETROLEUM REFINERIES (CLASSES 2, 3, and 4A)[1,2]

Classification[2]	Company	Site	Product[3]
2	Sunoco	Tulsa, OK	B, T
4A	Tenneco Chemicals, Inc.	Chalmette, LA	B, EB, T, X, OX, PX
4A	Texaco, Inc.	Port Arthur, TX	P, T
2	Texaco, Inc.	Westville, NJ	P, T
3	Texas City Refining	Texas City, TX	P
4A	Union Oil of California	Beaumont, TX	B, P, T, X
2	Union Oil of California	Lemont, IL	B, T, X
4A	Union Pacific Corp.; Champlin	Corpus Christi, TX	B, T, X

---

[1] This list was prepared under EPA contract 68-02-1319, Task 51, using information from the 1975 Directory of Chemical Producers and the April 7, 1975 issue of The Oil and Gas Journal. Modifications were made based on production sites for normal paraffins from A.V. Hahn, The Petrochemical Industry, p. 562.

[2] Class Two represents refinery associated company sites producing basic petrochemicals only and utilizing only separation techniques for the petrochemical production. An example of this category would be a refinery producing BTX by distilling these products from an aromatic rich stream.

Class Three represents refinery associated company sites which produce basic petrochemicals only, but also enhance feedstock yield by some initial processing (such as a refinery utilizing an olefins plant to increase ethylene/propylene production).

Class Four represents chemical production sites which produce both basic petrochemicals and industrial organic chemicals. This classification has been further subdivided with regard to refinery association such that Class 4A is a refinery associated site and Class 4B is not a refinery associated site.

[3] The following codes are used to indicate products produced at the site

AN	alkylnaphthalenes	N	naphthalene
B	benzene	NP	normal paraffins
BT	C_4 olefins & diolefins	OC	ortho-cresol
C	mixed cresols	OX	ortho-xylene
CA	cresylic acids	P	propylene
E	ethylene	PC	para-cresol
EB	ethylbenzene	PX	para-xylene
H	heptene	T	toluene
MX	meta-xylene	X	mixed xylenes

Table C-11. BASIC PETROCHEMICAL PRODUCTION SITES NOT DIRECTLY ASSOCIATED WITH A PETROLEUM REFINERY (CLASS 4B)[1,2]

Company	Site	Product[3]
Allied Chemical Corp.	Geismar, LA	E
American Cyanamid Corp	Boundbrook, NJ	PC
Arco Chemical Co.	Channelview, TX	BT, P, MX
Arco Chemical Co.	Wilmington, CA	B, E, P, T, X, NP
BASF Wyandotte Corp.	Geismar, LA	E, P
Chemplex Co.	Clinton, IA	E, P
Dow Chemical Co.	Bay City, MI	B, BT, E, P
Dow Chemical Co.	Freeport, TX	B, BT, EB, E, P
Dow Chemical Co.	Midland, MI	EB, T
Dow Chemical Co.	Plaquemine, LA	E, P
E. I. du Pont de Nemours & Co.	Orange, TX	E, P
Eastman Kodak Co.	Longview, TX	E, P
Foster-Grant Co., Inc.	Baton Rouge, LA	EB, T
GAF Corp	Joliet, IL	N
BF Goodrich Chemical Co.	Calvert City, KY	E, P
Gulf Oil Co.	Cedar Bayou, TX	BT, E, P
Jefferson Chemical Co.	Port Neches, TX	E, P
Kewanee Oil Co.	Solon, OH	N
Merichem Co.	Houston, TX	OC, C, CA
Monsanto Co.	Chocolate Bayou, TX	B, BT, EB, E, N, P, T, OX
Monsanto Co.	Texas City, TX	EB, E, T
National Distillers and Chemical Corp.	Tuscula, IL	E
Olin Corp.	Brandenburg, KY	E
Petrogas Producing Co.	Groves, TX	E, P
Petro-Tex Chemical Corp.	Houston, TX	BT
Productol Chemical Co.	Santa Fe Springs, CA	OC, C, CA
Shell Oil Co.	Dominguez, CA	P
Sherwin Williams Co.	Chicago, IL	PC
Standard Chlorine Chemical Co.	Delaware City, DE	N
Standard Chlorine Chemical Co.	Kearny, NJ	N

Table C-11.(Continued) BASIC PETROCHEMICAL PRODUCTION SITES NOT DIRECTLY ASSOCIATED WITH A PETROLEUM REFINERY (CLASS 4B)[1,2]

Company	Site	Product[3]
SunOlin Chemical Co.	Claymont, DE	E
Union Carbide Corp.	Penuelas, PR	BT, E, P, X
Unior Carbide Corp.	Seadrift, TX	BT, EB, E, P, T
Union Carbide Corp.	Taft, LA	B, BT, E, P, T
Union Carbide Corp.	Texas City, TX	BT, E, P, NP
Union Carbide Corp	Torrance, CA	E, P
Union Carbide Corp.	Whiting, IN	E, P

---

[1] This list was prepared under EPA contract 68-02-1319, Task 51, using information from the 1975 Directory of Chemical Producers and the April 7, 1975 issue of The Oil and Gas Journal. Modifications were made based on production sites for normal paraffins from A.V. Hahn, The Petrochemical Industry, P. 562.

[2] Class Two represents refinery-associated company sites producing basic petrochemicals only and utilizing only separation techniques for the petrochemical production. An example of this category would be a refinery producing BTX by distilling these products from an aromatic rich stream.

Class Three represents refinery-associated company sites whicn produce basic petrochemicals only, but also enhance feedstock yield by some initial processing (such as a refinery utilizing an olefins plant to increase ethylene/propylene production).

Class Four represents chemical production sites which produce both basic petrochemicals and industrial organic chemicals. This classification has been further subdivided with regard to refinery association such that Class 4A is a refinery-associated site and Class 4B is not a refinery-associated site.

[3] The following codes are used to indicate products produced at the site

AN	alkylnaphthalenes	N	naphthalene
B	benzene	NP	normal paraffins
BT	C_4 olefins & diolefins	OC	ortho-cresol
C	mixed cresols	OX	ortho-xylene
CA	cresylic acids	P	propylene
E	ethylene	PC	para-cresol
EB	ethylbenzene	PX	para-xylene
H	heptene	T	toluene
MX	meta-xylene	X	mixed xylenes